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AMERICAN
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*A Journal Devoted to the Instructional and Cultural Aspects of Physical Science*

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# Nuclear Magnetism*

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(Received July 16, 1953)

A review of modern developments in magnetism with special attention to the magnetic effects in gross matter that have their origins in the magnetic moments of nuclei.

IN the ninth Richtmyer Lecture three years ago, Professor Van Vleck spoke on Landmarks in the Theory of Magnetism.[1] What I have to say is really only another chapter in that story. It has to do with the magnetic effects in matter that have their origin in the magnetic moments of nuclei. Many of the topics I shall touch on could appropriately appear in a lecture with some other title—Nuclear Moments, Nuclear Resonance, Nuclear Induction, or even Radio-frequency Spectroscopy. Lectures so entitled have not been rare, and informative review articles can be found in several places, including the *American Journal of Physics*.[2] But it may be worth while to look at the subject in the large, and from a point of view that one is not likely to adopt when one is trying to understand a particular class of experiments. I suggest that we examine the subject solely as a topic in magnetism, pursuing as far as possible the parallels with ordinary—that is, electronic—magnetism, and trying to pin down essential differences where we may find them. Let us, if you will, try to anticipate a section in some future edition of Van Vleck's *Electric and Magnetic Susceptibilities* (a book that was itself a landmark in the theory of magnetism). It is perhaps not too soon to take this step, for parts of the field are already being taken over by chemists, a development that may indicate some degree of maturity in the subject.

Let us recall the main features of magnetism in matter, a subject the student always finds divided in three parts, diamagnetism, paramagnetism, and ferromagnetism. Diamagnetism occurs in all substances, lends itself readily to a superficial explanation, and reveals its true subtlety only on close inspection. It will come into our story indirectly, later on. Ferromagnetism, that remarkable accident in the periodic table, involves what we have learned to call a cooperative phenomenon. All the elementary magnets in a macroscopic bit of matter conspire to align themselves through mutual interaction. The nuclear analogue of this behavior would be a very interesting effect, needless to say, but it has not been found. We should at least inquire presently whether conceivable conditions could bring it about.

Our real point of departure is of course paramagnetism, in which the elementary mag-

* The twelfth Richtmyer Memorial Lecture of the American Association of Physics Teachers, delivered at the twenty-second annual meeting, Cambridge, Massachusetts, January 23, 1953.

[1] J. H. Van Vleck, Am. J. Phys. **18**, 495 (1950).

[2] G. E. Pake, Am. J. Phys. **18**, 438 and 473 (1950).

nets are aligned by a external magnetic field, but only partially aligned because of the continual disturbance of thermal agitation. Electronic paramagnetism and nuclear paramagnetism are explained in exactly the same way. One assumes he has a collection of $N$ elementary magnetic dipoles, each of strength $\mu$, subjected to a magnetic field **H**. The orientation of each dipole with respect to the field is limited to certain few possibilities, depending on the angular momentum **Ih**, associated with the dipole. One describes this situation by saying that there are $2I+1$ energy levels for each dipole. If one calculates the equilibrium populations of these levels, corresponding to a temperature $T$ for the whole system, he finds that the levels of lower energy (orientation more nearly in the direction of the field) are favored to just such an extent that the whole specimen ought to acquire a magnetic polarization

$$M=NH(\mu^2/I^2)I(I+1)/3kT. \qquad (1)$$

At least, this will be the result if the field is not too strong. If $N$ is reckoned for one cm$^3$, the corresponding magnetic susceptibility is

$$\chi_0=\frac{N}{3kT}\cdot\frac{\mu^2 I(I+1)}{I^2}. \qquad (2)$$

This is the theoretical expression of Curie's Law; the static susceptibility is inversely proportional to the absolute temperature.

We have only to put in for $\mu$ an electronic moment, or a nuclear moment, depending on our interest. Now nuclear moments are generally about a thousand times smaller than electronic moments, so nuclear paramagnetism is a pretty feeble effect. The nuclear susceptibility of water at room temperature is about $3\times10^{-10}$. To a student of a practical turn of mind, that is not very striking, for he would already have dismissed electronic paramagnetism as a rather academic topic. But for an experimenter who wants to observe and measure nuclear paramagnetism, the factor $(1/1000)^2$ creates a formidable problem. It was indeed an experimental triumph when, in 1937, Lasarew and Schubnikow succeeded in measuring the nuclear paramagnetic susceptibility of solid hydrogen.[3]

[3] B. Lasarew and L. Schubnikow, Physik. Z. Sowjetunion 11, 445 (1937).

To take advantage of the $1/T$ in Curie's Law, they cooled their frozen hydrogen to 2°K, where the nuclear susceptibility was no longer completely swamped by the normal electronic diamagnetism. The nuclear magnetization was detected in a satisfyingly direct manner, through the force on the specimen in an inhomogeneous field. (Fig. 1).

So far as I know, no similar experiment has since been reported. There are two good reasons for this rather curious state of affairs. In the first place, it has turned out that nuclear paramagnetism is much more easily investigated through the phenomenon of resonance, a word that was bound to come into this discussion before long. In the second place, there has been no reason to expect interesting departures, in the static nuclear susceptibility, from the simple behavior predicted by Curie's Law. This is in sharp contrast to the situation in electronic paramagnetism. Here is one difference between electronic and nuclear magnetism that is worth a closer look.

As you will remember, electronic paramagnetism is not nearly as simple as my off-hand explanation of Curie's Law might suggest. For one thing, there is the phenomenon of saturation. Equation (1) is only a limiting case of a more general formula. The polarization of the specimen can obviously never exceed the value that corresponds to complete alignment of the elementary magnets, however strong the field. Saturation effects will become noticeable, generally speaking, when $\mu H$, the orientation energy, becomes comparable to $kT$. With electronic moments, such a condition can be reached at reasonable field strengths at temperatures of a few degrees Kelvin. For a typical nuclear magnetic moment, however, $\mu H\approx kT$ implies that $H/T$ is at least $10^7$ gauss/deg. At 0.01°K, for example, we need a field of 100 000 gauss to bring about anything approaching complete nuclear alignment, or magnetic saturation. A considerable effort to attain such conditions is now under way in several places. A group working with Professor Simon at Oxford appears to be rather close to the goal. There are two reasons for trying to produce a high degree of nuclear alignment: first, to study the directional properties of nuclear radiation; second, as a

starting point for nuclear adiabatic demagnetization, by which it may be possible to reach temperatures in the range of a millionth of a degree. In that range nuclear magnetism will come into its own as the dominant thermodynamic property of matter. But this has taken me away from my point, which is that under ordinary conditions, saturation plays no role in nuclear paramagnetism.

A more subtle complication in electronic paramagnetism arises from the magnetic fields the elementary magnets exert on one another. The effective aligning field is not merely the field we apply from the outside, but includes the local field due to the existing polarization of the specimen. This should call to mind Lorentz's model of the dipole in the cavity, as well as the analogous and equally troublesome problem in the theory of dielectrics. The problem in this form hardly arises in nuclear paramagnetism because the local field is so weak. Even if the nuclei were polarized to saturation, the local field would be only a small fraction of the field we could apply with a magnet.

Some electronically paramagnetic substances flagrantly violate Curie's Law for quite a different reason. The magnetic moment of an atom or molecule—what I have been calling an "elementary magnet"—has in general two sources, the intrinsic magnetic moment associated with electron spins, and the magnetic moment of electron orbits. For given total orbital angular momentum $\mathbf{L}$ and spin angular momentum $\mathbf{S}$, there are several possibilities for the combination $\mathbf{L}+\mathbf{S}$, with differing total magnetic moments. Spin-orbit coupling separates these possible states in energy—the familiar spin multiplet of spectroscopy. If the levels of the multiplet happen to be separated by an energy difference comparable to $kT$, a change in temperature will bring about a redistribution over the levels, with an accompanying change in the effective magnetic moment. It is not surprising that Curie's Law fails in this situation. Now what would be the precise nuclear analog of this behavior? The nuclear moment too, in many cases, is made up of a spin and orbital contribution, the orbital part arising from the motion of charge within the nucleus. The success of the shell theory of nuclear structure gives us considerable confidence in using such language. In fact, one speaks of spin-orbit coupling and spin-multiplets in the nucleus. But of course there is one big difference: the multiplet splittings are here on the scale of nuclear binding energies. They are bigger than $kT$ by an enormous factor—unless you want to consider temperatures of the order of $10^8$ degrees; paramagnetism at $10^8$ degrees is indeed an academic topic! There is thus not much prospect of finding, in nuclear paramagnetism, the revealing aberrations that spin-multiplets cause in electronic paramagnetism.

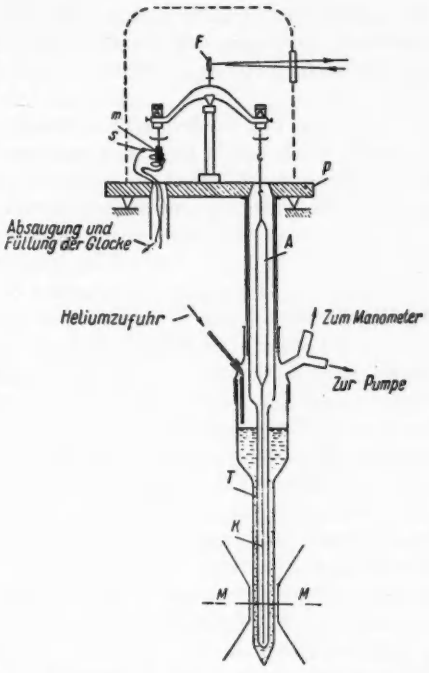


FIG. 1. Apparatus used by Lasarew and Schubnikow in 1937 to detect nuclear paramagnetism in solid hydrogen. The hydrogen was frozen in the long capillary $K$.

Another effect has come in for a good deal of attention in modern theories of magnetism, the effect of internal electric fields on the electron orbits in a crystal. These fields in crystals often have a drastic effect on the orbital contribution to the magnetic moment, sometimes removing, or "quenching" it altogether. The exact nuclear analog of this effect seems to be outside our present experimental grasp, but perhaps it will not remain so. The difficulty is that the nucleus

is so tightly put together that electric field gradients of the magnitude found in atoms and molecules perturb its structure only very, very slightly.[4]

One can, however, think of an effect in nuclear magnetism which would be *almost* analogous to the crystalline Stark effect in ordinary paramagnetism. Consider the free hydrogen molecule $H_2$, in a particular rotational state. Let it be an *ortho*-hydrogen molecule, so that the total nuclear spin is 1. The magnetic moment of the molecule is made up of two parts, a part due to the combined moment of the two protons, and a moment arising from the molecular rotation. This last is not out of place in a neutral molecule—it simply happens that the current loop represented by the revolving protons is not wholly compensated by the motion of the electron cloud. These facts are all well known from molecular beam experiments on hydrogen molecules. Both magnetic moments, nuclear and rotational, would play a role in determining the static magnetic susceptibility of hydrogen gas, for example. If you were to calculate how they should combine, you would find yourself repeating, in essence, the calculation of the susceptibility of an atom with electron orbit and spin moments. In crystalline hydrogen however, we have clear evidence that the rotational levels are split by the crystalline field, and that the rotational moment is in fact "quenched," in a manner quite analogous to the quenching of orbital moments in a paramagnetic crystal. I think it is a safe bet that somewhere between room temperature and 2°K, say, the static susceptibility of hydrogen will deviate from Curie's Law. Unfortunately, to demonstrate it directly would require a measurement much more delicate than that of Lasarew and Schubnikow.

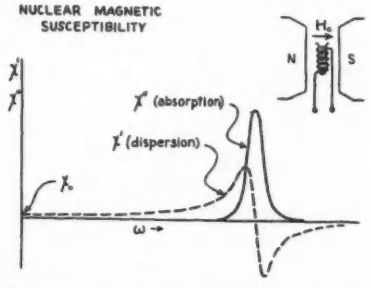


FIG. 2. Paramagnetic susceptibility as a function of frequency. The graph is *not* in correct proportion; the absorption peak is *much* higher and much narrower than here shown, in the nuclear case.

[4] Distortion of the electric charge distribution in the nucleus by molecular electric fields, may actually be observable. See Gunther-Mohr, Geschwind, and Townes, Phys. Rev. **81**, 289 (1951); but see also Wang, Townes, Schawlow, and Holden, Phys. Rev. **86**, 809 (1952).

For practical purposes then, the nucleus is the ideal elementary magnet that we have always told our students about, and nuclear magnetism seems to have been designed as a textbook example of Curie's Law. In fact we have had to strain our imagination to conceive of circumstances in which departures from Curie's Law might be detectable. This is a great pity, for it means that we can hardly hope to learn about nuclear structure from nuclear paramagnetism in the way we have learned things about atomic and molecular structure from electronic paramagnetism.

The prospect is not so barren, however, if we look in another direction. We have lingered too long around the origin, and it is time to move out along the frequency axis. Instead of the static susceptibility $\chi_0$, we examine the susceptibility in an alternating field, of frequency $\omega$, in the presence of a strong constant field $H_0$. As a function of frequency, the susceptibility of an electronic paramagnet and that of a nuclear paramagnet behave very much alike. Figure 2 could serve for both. We plot here (not to scale) the real and imaginary parts of the magnetic susceptibility, that is, the *dispersion* and the *absorption*.

The conspicuous resonance occurs, as I hardly need explain, at a frequency that corresponds to the spacing of the Zeeman levels associated with different orientations of the elementary magnets in the strong field $H_0$. An equivalent description can be given in terms of the precession of a magnetic top. By measuring the magnetic field and the resonance—or precession—frequency, we can determine the magnetic moment of the elementary magnet to its angular momentum. Incidentally, at resonance the susceptibility $\chi''$ is greater than the static susceptibility $\chi_0$ very nearly in the ratio of frequency to resonance width. This is an example of a general rule that shows up in many disguises. You may have met

it when working with electric circuits, light waves, or even slow neutrons. Here the multiplication factor can be very large; it is often several thousand and sometimes nearly a million. This is one reason for the great advantage of resonance experiments over static measurements, in electronic as well as nuclear paramagnetism.

In a typical nuclear case, a field of a few thousand gauss may bring the resonance into the neighborhood of a few megacycles per second. In the same field, the electronic resonance would fall in the microwave part of the spectrum. That may help to explain why electronic resonance was not observed until after the war, whereas Rabi had demonstrated and exploited nuclear resonance in molecular beams in 1938. Recent work in paramagnetic resonance has uncovered several instances in which the electron resonance is rather easily detectable at low fields and frequencies, which only goes to show that it is easier to find things after you have learned how to look for them. Actually, the outbreak of resonance experiments after the war, including these in nuclear resonance, must be attributed in part to our wartime lessons in how to make the most of electronic amplification—"signal-to-noise," and all that. Nor ought I to leave the impression that, on the conceptual side, the approach followed the line I have adopted in this lecture. The idea of resonance transitions, and the vivid picture of the classical analog, the precessing magnetic top—both popularized by the molecular beam experiments—seem to have been the inspiration in most cases.

To get back to the physics of the problem before us, the width and shape of the resonance line, and some other less obvious features of the phenomenon, are governed by the interactions of the elementary magnets with each other and with their surroundings. Speaking broadly, these interactions are *strong* in the electronic case and *weak* in the nuclear analog. But there are other essential differences.

Interatomic electric fields act directly on electron orbits and indirectly, through spin-orbit coupling, on the electron spins themselves. If these fields vary in time, because of thermal vibrations perhaps, their action may so disturb the peaceful occupation of the Zeeman levels that the electronic resonance line is much broadened. Another important perturbation is the purely *magnetic coupling* of one atomic dipole to its neighbor. Finally, there is the effect of *electron exchange*, which plays so decisive a role in ferromagnetism. In electronic paramagnetism, exchange has the curious, but welcome effect of sharpening up the resonance line. It is almost as if the electrons were wandering freely through the crystal, so that two neighboring spins never spent long enough together to disturb one another.

Now let us look at the nuclear paramagnetic substance. To find an example of a nuclear paramagnet, by the way, we do not have to order chemicals like rare earth salts. An ordinary ice cube will do, or almost anything else you can lay your hand on. What are here the important interactions? Exchange we can at once dismiss. It does not occur to any appreciable extent simply because the nuclear wave functions of two adjacent atoms practically do not overlap.

The rapidly fluctuating magnetic fields arising from disturbances in the electron cloud, and even from motion of the nucleus itself, have practically no effect on the nuclear magnetic moment. They vary too rapidly, and this brings up a point which is really central to our understanding of nuclear magnetism. Any field that is going to have an effect on nuclear resonance must have a static component, or it must vary at some frequency in the neighborhood of the nuclear resonance frequency—that is at some few million cycles per second. Now that is a very low frequency to look for in the atomic domain. Even the thermal vibrations of the crystal are dominantly at very much higher frequencies. There is plenty of electromagnetic noise in a crystal, but it is all pretty shrill—the nuclear magnet, tuned to a very low note, doesn't hear much of it.

About the only thing left, in this simple case, is the action of the nuclear magnetic dipoles on one another. One proton in an ice crystal produces at its neighbor a field of a few gauss, which has not only a static component but an oscillating component that is practically in resonance with its neighbor's precession. This is the dominant cause of line broadening in many common cases. Figure 3 shows some nuclear resonance lines whose widths and shapes are determined wholly

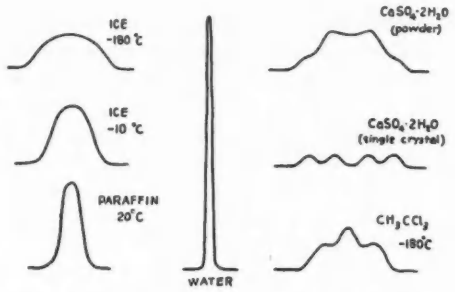


FIG. 3. Some typical line shapes in nuclear resonance absorption. Absorption is plotted as a function of field $H_0$ at constant frequency $\omega$, or as a function of $\omega$ at constant field. In each of the examples shown it is the proton resonance that is being observed.

by the magnetic dipole-dipole interaction. You will notice that some of the lines show a complex structure. This is typical of situations in which two or three magnetic nuclei lie close together in a group. From the observed structure one can deduce the dimensions of the group, and in a single crystal one can tell something about the orientation of the group in the lattice. This effect, discovered by Pake, is one of the aspects of nuclear magnetism that has turned out to interest physical chemists—or at any rate chemical physicists.

In water, and in fact in any reasonably fluid substance, including gases, the dipole-dipole interaction is nearly wiped out because the motion of the molecules interrupts it so frequently. Each nuclear dipole is then left practically free of all disturbances, and the result is an extraordinarily sharp and intense resonance line. This is a happy result in two ways. It makes possible extremely precise measurements of nuclear moment ratios, and it permits the study of certain much weaker effects which would otherwise have been masked by the dipole-dipole interaction.

Any very great increase in resolving power is likely to disclose new effects. That is an old story in physics. We remember that the magnetic moment of the nucleus was itself discovered through the hyperfine structure of lines in the visible spectrum. As soon as it was understood why the nuclear resonance line in liquids was so narrow, it was clear that the only practical limit on resolution was the inhomogeneity of the magnetic field applied to the specimen. Efforts were made in several laboratories to improve the magnets. With the improved resolution it was soon found that identical nuclei, in the same applied field but in chemically different molecules, do not precess at exactly the same frequency. Knight at Brookhaven and Dickinson at Massachusetts Institute of Technology were the first to study this effect. The explanation is simple: the magnetic field at the atomic nucleus differs slightly from the field applied because of the diamagnetic shielding effect of the electron cloud around the nucleus. In different molecules the atom's electron configuration will differ slightly reflecting differences in the chemical bond. The resulting displacement of the resonance line is called a "chemical shift." It is only a nuisance to the experimenter interested in the exact ratios of magnetic moments. But it is interesting to the chemist because it reveals something about the electrons that partake in the chemical bond.

A striking, and now famous example of this effect is shown in Fig. 4. This example was discovered at Stanford by Packard and Arnold. It is the proton resonance in ethyl alcohol, seen under very high resolution. Each line comes from a chemically significant group of protons in the molecule, the intensity being proportional to the number of hydrogen atoms involved, 3 (methyl group), 2 ($CH_2$ group), and 1 (hydroxyl), respectively.

This is not the only subtle effect that has come to light. One of another sort first turned up in the ingenious spin-echo experiments of E. L. Hahn, and is seen in its simplest form in Fig. 5. This shows the nuclear resonance in the gas HD,

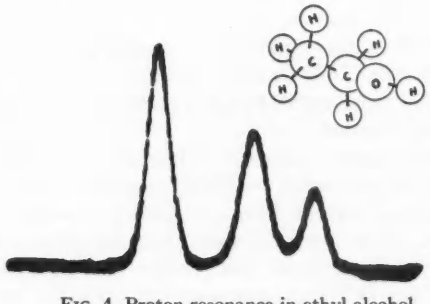


FIG. 4. Proton resonance in ethyl alcohol (Packard and Arnold.)

as observed by T. E. Wimett of Massachusetts Institute of Technology. Dr. Wimett has pushed to new heights of precision the comparison of magnetic moments of the proton and the deuteron. With the resolution he achieved, the proton line appears as a triplet and the deuteron line as a doublet. This splitting does not arise from any effect on the applied field, but from an indirect coupling of the proton to the deuteron through the medium of the two electrons in the hydrogen molecule. The splitting amounts to 43 cycles per second, and is as much an intrinsic property of the HD molecule as any line in its optical spectrum. I am sure we have only begun to explore the domain of very weak interactions—the "audio spectrum" of molecules if I may call it that.

There is a whole family of effects in nuclear magnetism, with no close analog in electronic magnetism, effects of the nuclear electric quadrupole moment. Every nucleus with spin greater than $\frac{1}{2}$ has a quadrupole moment, which is a way of saying that its charge distribution is not, in general spherical. It therefore experiences a torque in an inhomogeneous electric field, very much as our nonspherical earth experiences a torque in the nonuniform gravitational field of the moon and sun. The equivalent of the precession of the equinoxes is here the precession of the nuclear axis in the electric field in a molecular crystal. It has the effect of splitting the nuclear resonance line, first discovered by Pound, and exemplified in one of his records reproduced in Fig. 6. This is the sodium resonance in $NaNO_3$. In the complete absence of a magnetic field, we still have a sharp resonance associated with quadrupole coupling, the pure quadrupole resonance discovered by Dehmelt

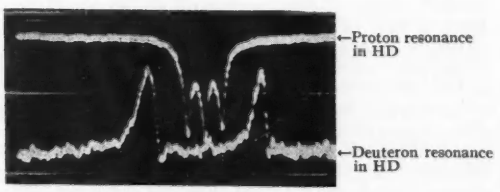


FIG. 5. Simultaneous traces of the proton resonance in HD and the deuteron resonance in the same sample. The sample is a gas under high pressure. (Courtesy of T. E. Wimett.)

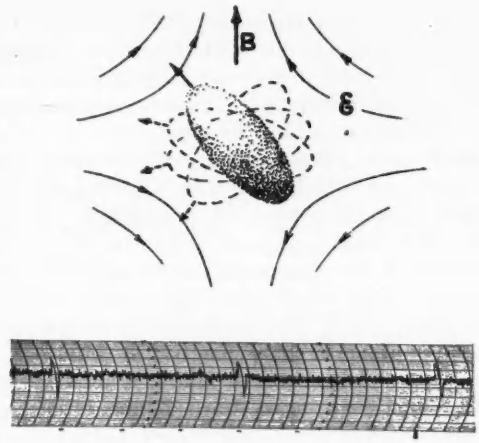


FIG. 6. An elliptical charge distribution in an inhomogeneous electric field (above) and the sodium resonance in $NaNO_3$, showing a triplet structure caused by the interaction of the electric quadrupole moment of $Na^{23}$ with the electric field in the crystal (R. V. Pound).

and Krüger in Göttingen. Whether this can be called nuclear magnetism or not I do not know. At any rate, it is a lively subject, and we have had one whole session in this meeting devoted to it.

In both electronic and nuclear paramagnetism one meets the question of *relaxation*. This word refers to the way or ways in which the magnetic energy of the system is passed along as heat to the atomic surroundings. The term relaxation is also applied to the exchange of energy among the elementary magnets themselves, but I shall not use it that way here. If we think of the elementary magnets themselves as a system in the thermodynamic sense of the word, connected by a heat-conducting link to the world around them, we are concerned with the effectiveness of this link—to be specific, with its "time constant." How long will it take the elementary magnets —"spins," for short—to come to thermal equilibrium if we suddenly change their temperature, or the temperature of their surroundings? In electronic paramagnetism this "relaxation time" is of the order of $10^{-6}$ to $10^{-9}$ second. In the nuclear magnetism, times as short as $10^{-4}$ second, and as long as a few hours, have been observed.

A property that can vary by a factor of $10^8$ is apt to be interesting, and relaxation phenomena

have been both fascinating and puzzling. The problem is an old one in electronic paramagnetism, going back to the experiments of Gorter in the thirties. But in the electronic case it has been sadly complicated by the strong interactions to which the electrons are subject. We have made rather rapid progress in understanding nuclear spin relaxation, first, because much of the essential theory was ready at hand, having been developed for electronic paramagnetism by Waller, Van Vleck and others, and second, because nuclear magnetism really presents a cleaner problem. It is too bad it wasn't discovered first. However, I think it is fair to claim that what we have learned about nuclear relaxation has, by way of return, thrown some light on electronic relaxation. And it has also provided a very sensitive and quantitative indicator of internal motion in crystals and fluids, rubber and surface catalysis.

The course we have been following brings us eventually to the question of nuclear ferromagnetism and diamagnetism—if any. Could the nuclear magnetic dipoles in a substance spontaneously line up? We remember that exchange coupling is here quite insignificant. But we do have the purely magnetic coupling of neighboring dipoles, which is of a rather different character. A necessary, if not sufficient, condition for spontaneous alignment is that this coupling energy shall be comparable to $kT$. This implies, if you will put in the numbers, that a temperature around $10^{-7}$ °K or lower will be needed. Now this is just the range that one might hope to reach by adiabatic nuclear demagnetization, so there is some hope that the question may some day be put to the test. The result will be very interesting, for there is a theoretical puzzle of long standing about the eventual cooperative behavior of a pure dipole lattice. Perhaps the nuclear magnet will become antiferromagnetic.

As to whether there is a nuclear analog of electronic diamagnetism, I think I shall leave that as a question for the student. I do so for the good, and not unprecedented, reason that I am not prepared to answer it. The student's first problem is to decide what the question means.

This comparison of electronic and nuclear magnetism may have seemed a bit forced here and there, but that is only because the parameters of the problem are so different. The basic physical notions are very much the same. It was my hope that in comparing the two phenomena point by point, we might be led to ask ourselves questions we had not thought of asking before. We all know, as teachers, that that can be a fruitful occupation.

## The Tape Recordings of Important Speeches

BY

E. U. CONDON, K. K. DARROW, E. FERMI, J. C. SLATER

Free tape recordings are available on loan to members of the Association who wish to use them for presentation to classes, seminars, or science clubs. The subjects are four of the six lectures presented as a Symposium on Physics Today at the Twentieth Anniversary meeting of the American Institute of Physics, Chicago, Illinois, on October 25, 1951, as follows:

**The atom.** E. U. CONDON.

**Physics as science and art.** K. K. DARROW.

**The nucleus.** E. FERMI.

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# The Uncompensated Pendulum Clock

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(Received May 20, 1953)

From the teaching standpoint in general physics, the pendulum clock uncompensated for temperature change continues to offer valuable material. The present discussion emphasizes that although the oscillation rate is affected by thermal expansion or contraction, causing the clock to "lose" or "gain," the behavior of the clock remains perfectly normal, that is, "correct," controlled by physical laws. Consequently, the terms "correct" and "incorrect" should not be applied to period or temperature, but such terms as "standard" or "nonstandard" substituted for them. Attention is focused on the sharp distinction between indicated and actual elapsed time, with *indicated seconds per vibration*, a constant of the clock, as the key to a clear and general analysis. This constant equals the period only at the standard temperature.

IN general physics, a good problem in thermal expansion is that of an uncompensated pendulum clock, where, for example, the question is asked, "what are the temperature limits between which the clock will not 'gain' or 'lose' more than a specified number of seconds per day?" Students in a current pre-engineering physics course had special difficulty with it. Meeting it for the first time as a student, I got a numerical answer which agreed well enough with the book. However, there remained a feeling of uneasiness as to exactness of the working method. Moreover working the problem on the basis of a "seconds pendulum" left a feeling of not enough generality. Actually, the same answer is obtainable no matter what is the assumed rate of swing of the clock pendulum when running "correctly."

## CLOCK'S PERFORMANCE IS ALWAYS "RIGHT"

Uncertainty here can be avoided. The clock's performance is faithful. The laws of mechanics and the property of thermal expansion determine how the pendulum behaves. There is nothing whatever abnormal about the clock's running "fast" or "slow." As a parallel case, ray aberrations in an optical instrument, however undesirable, are normal, a consequence of the law of refraction. As to the pendulum, according to the existing temperature its period, frequency of vibration, and *indicated* elapsed time during any given interval of actual time, say one day, are all of them what one should expect.

I believe that the terms "correct" and "incorrect" should not be applied here to period, frequency, or temperature.[1] (Incidentally, while its running rate responds to temperature change, the clock is unconcerned with the idiosyncrasies of particular thermometers.) The "error," of which the clock is wrongly accused, has a subjective nature. The person reading it simply mistakes the value of the *indicated* for the actual time.

## CLEARNESS FROM DEFINITE THINKING

The most important quantity which the student should consider is, I think, the indicated seconds per vibration $K$. This constant is independent of the running rate. It equals the *period* of the pendulum only when the clock is running at the particular temperature at which it indicates the actual elapsed time, as given by some "master clock." This particular temperature will be referred to as "standard."

Also, the reciprocal of $K$ is, of course, a constant of the clock; *viz.*, the number of vibrations per *indicated* second, which likewise is

[1] A search of the literature has not shown quite the same attitude toward the pendulum clock. For those interested in the general subject of pendulums, a concise list of articles on and references to pendulums of various types, variously treated, will be found in the *American Journal of Physics* as follows: J. A. Van den Akker, **3**, 72 (1935); Karl D. Larsen, **5**, 130 (1937); I. Walerstein, **7**, 190 (1939); W. W. McCormick, **7**, 260 (1939); Philip A. Constantinides, **7**, 417 (1939); Willoughby M. Cady, **10**, 114 (1942); Yee-Tak Yu, **10**, 152 (1942); M. J. W. Phillips, **10**, 217 (1942); Park Hayes Miller, Jr., **13**, 40 (1945); Albert Burris and W. J. Hargrave, **13**, 215 (1945); P. L. Tea, **13**, 245 (1945); Mario Iona, Jr., **14**, 255 (1946); John Satterly, **14**, 316 (1946); T. A. Benham, **15**, 285 (1947); Eric J. Irons, **15**, 426 (1947); Seville Chapman, **16**, 308 (1948); Ancil Thomas, **19**, 196 (1951); Harold P. Knauss and Paul R. Zilsel, **19**, 318 (1951); Julius Sumner Miller, **21**, 315 (1953).

independent of the running rate. This reciprocal equals the *frequency* of the pendulum only when the clock is running at the standard temperature.

## ANALYSIS AND SOLUTION OF THE PROBLEM

The problem may be worked as follows. Assume an ideal, or simple, pendulum of any length, with a stated tolerance of $\pm 1$ second per day, or 86 400 sec, which we shall call the "reference time interval." That is, the clock is permitted to gain or lose no more than that. Let $t_0$, $t$ be the standard temperature and any other temperature, and $L_0$, $L$ the corresponding lengths of the pendulum. At the standard temperature the *indicated* time is equal to the actual elapsed time. Since the period $T=2\pi\sqrt{(L/g)}$, we have as the ratio of the two periods $T/T_0=\sqrt{(L/L_0)}$, and since $L=L_0(1+\alpha\Delta t)$, where $\Delta t=t-t_0$, we get

$$T/T_0=\sqrt{(1+\alpha\Delta t)}, \tag{1}$$

showing that the percentage change of period is independent of $L_0$, the pendulum length at the standard temperature.

In Eq. (1), $\alpha$ is defined by $[(L-L_0)/L_0]/\Delta t$, which is the relative change in length per unit temperature change. As is usually done in problems of thermal expansion where the range of temperature is not too great, the rate of change of length with temperature $dL/dt$ will be regarded in this paper as constant, which it is only approximately.[2] The value of the derivative depends on the initial length chosen at the standard temperature, or in other words, on the standard temperature chosen for a given sample of the material. We shall come back to this point later in the paper.

If one expresses the length $L$ at a given temperature $t$, with the thermal-expansion formula, using first $t_0$ and then any other temperature $t_1$ as another reference, or standard, temperature, and eliminates $L$ between the two equations, substituting $L_1=L_0[1+\alpha_0(t_1-t_0)]$, there results $\alpha_1=\alpha_0/[1+\alpha_0(t_1-t_0)]$, showing that $\alpha_1\neq\alpha_0$. Note also that $\alpha_1$ like $\alpha_0$ depends only on its own reference temperature.

[2] A detailed discussion of the variability of the linear expansion coefficient $\alpha$ with temperature is included in an article by Hitchcock and Zemansky, Am. J. Phys. **13**, 329–333 (1945).

To proceed with the analysis of the problem, the actual elapsed time for one day is independent not only of $L_0$ but also of the running rate of the clock. Let $n$ be the total number of vibrations the pendulum makes in one day, or 86 400 seconds. Then $n_0=86\,400/T_0$, and $n=86\,400/T$. These equations combined give

$$T/T_0=n_0/n. \tag{2}$$

From Eqs. (1) and (2),

$$n_0/n=\sqrt{(1+\alpha\Delta t)}. \tag{3}$$

Here we introduce a constant of the clock $K\equiv T_0$, its *indicated* seconds per vibration. Then $nK$ is always the total *indicated* time for one day. In the given problem, $n_0K=86\,400$ sec, while $nK=(86\,400\pm 1)$ sec. Obviously the plus sign applies where $t<t_0$, the temperature having fallen, $\Delta t$ being negative and the pendulum thereby shortened, so that the clock runs faster than at the standard temperature, whereas the minus sign stands for the opposite case. If we combine these two equations we get

$$n_0/n=86\,400/(86\,400\pm 1). \tag{4}$$

Then by Eqs. (3) and (4),

$$\Delta t=\{[86\,400/(86\,400\pm 1)]^2-1\}/\alpha, \tag{5}$$

from which comes the required numerical result.

## NUMERICAL ANSWER

For the positive sign in Eq. (5), the indicated time is greater than at standard temperature; the pendulum has shortened because the temperature is below standard; and $\Delta t[\equiv(\Delta t)_1]$ is negative. Similarly, for the minus sign $\Delta t[\equiv(\Delta t)_2]$ is positive.

The arithmetic here goes beyond a pocket slide rule. With a brass pendulum, given $\alpha=2.0\times 10^{-5}(°\text{C})^{-1}$, the permissible temperature range is found to be $(t_0-1.16)$ to $(t_0+1.16)$°C. Note that, practically, to three figures the standard temperature is midway between the two limits. But strictly, $|(\Delta t)_1|\neq|(\Delta t)_2|$, as the ratio of these two quantities shows. Letting $c$ be the reference time interval, we get

$$\begin{aligned}(\Delta t)_1/(\Delta t)_2[\equiv Z] &= -[(2c+1)/(2c-1)]\cdot[(c-1)/(c+1)]^2\\ &= -(2c^3-3c^2+1)/(2c^3+3c^2-1)\\ &\doteq (2c-3)/(2c+3). \end{aligned}\tag{6}$$

Numerically, in the present problem, since $c=86\,400$ sec, $Z=-0.999\,965\,2$, which is almost, but not quite, equal to unity.

## GENERALIZED SOLUTION

In order to broaden the analysis, proceeding "inductively" we may use any number of seconds $\tau$ as the tolerance for any reference time interval $c$. (In the problem above, $c=1$ day, while $\tau=\pm 1$ sec.) Equation (3) remains as before, $n_0/n=(1+\alpha\Delta t)^{\frac{1}{2}}$. As above, $c=n_0T_0$ $[\equiv n_0K]$, and the indicated time in any case is $nK\equiv nT_0=c(1+\alpha\Delta t)^{-\frac{1}{2}}$. The "tolerance," that is, the difference between the maximum or minimum indicated time and the correct time is, $\tau=nT_0-c$ $\equiv nK-c$, which by Eq. (3) becomes

$$\tau=[(1+\alpha\Delta t)^{-\frac{1}{2}}-1]c. \tag{7}$$

Now $\Delta t$ the temperature difference from standard may be either positive or negative so that, $\alpha$ being positive, the quantity $(1+\alpha\Delta t)$ may be either $>1$ or $<1$. For the practical range of temperatures here, $|\alpha\Delta t|<1$. The square-root term will not be imaginary. In the algebraic $\pm$sign before the radical, the negative has no physical meaning here, any more than before the radical in the equation for the pendulum period with which we started. Consequently, since $c$ is positive, the difference $\tau$ will be plus or minus depending on the value of the radical term relative to unity, in Eq. (7).

Obvious interpretations in Eq. (7) may be tabulated as in Table I.

If the tolerance $\tau$ be regarded always as a positive quantity, Eq. (7) becomes

$$\tau=\pm[(1+\alpha\Delta t)^{-\frac{1}{2}}-1]c. \tag{7a}$$

Corresponding to Eq. (5) in the problem above, we have from (7a),

$$\Delta t=\{[c/(c\mp\tau)]^2-1\}/\alpha; \tag{7b}$$

$$c=\mp\tau/[(1+\alpha\Delta t)^{-\frac{1}{2}}-1]. \tag{7c}$$

In Eqs. (7 a, b, c) it is understood that the upper sign is to be used if $\Delta t$ is negative, the lower sign if it is positive.

From Eq. (7b) a practical working equation is obtained by neglecting the amount of the tolerance $\tau$ compared with the magnitude of $c$,

TABLE I. Significance of Eq. (7).

| $\Delta t$ | Pendulum $L$ | Swing rate | $\tau$ | Clock |
|---|---|---|---|---|
| neg. | $<L_0$ | "fast" | pos. | "gains" |
| 0 | $=L_0$ | desired | 0 | is "right" |
| pos. | $>L_0$ | "slow" | neg. | "loses" |

so that Eq. (7b) becomes

$$\Delta t=\pm 2\tau/(\alpha c), \tag{7d}$$

which applied to the problem above gives $\Delta t=\pm 1.16$, as before. The approximation in Eq. (7d) makes $|(\Delta t)_1|=|(\Delta t)_2|$.

From Eq. (7b),

$$(\Delta t)_1/(\Delta t)_2=-[(2c+\tau)/(2c-\tau)]\cdot[(c-\tau)/(c+\tau)]^2, \tag{8}$$

corresponding to Eq. (6) above.

The percentage difference of the absolute value of this ratio from unity is

$$200\tau(\tau^2-3c^2)/[(2c-\tau)(c+\tau)^2], \tag{8a}$$

or neglecting $\tau$ compared with $c$, this becomes $-300\tau/c$ percent, which is a much simpler expression and in the problem above has the value 0.0035 percent. The mathematical error in percent between this approximation and the exact Eq. (8a) is

$$100\tau[3\tau^2-c(2\tau+9c)]/[2c(\tau^2-3c^2)]. \tag{8b}$$

Neglecting $\tau$ compared with $c$, we get $150\tau/c$ percent, which in the problem above is 0.0017 percent, which incidentally is half the preceding approximate error.

## PHYSICAL PENDULUM

The present problem has been treated here as though the clock had a simple pendulum. But this has no physical existence, since it is only a concept. All actual pendulums are physical, not simple in the ideal sense. Will Eq. (5) apply to a physical pendulum regarded as being replaced by the equivalent simple pendulum? Specifically, let the clock pendulum be a bar of uniform rectangular cross section, oscillating about the upper end. Another question: is Eq. (5) valid regardless of uniformity of the bar, that is, must the distribution of matter in the pendulum be taken into account?

### CHANGE IN $g$

A corresponding problem with a pendulum clock regards the length as constant but the altitude, that is, g, variable, affecting the running rate. If we proceed as above, $T/T_0=\sqrt{(g_0/g)}=n_0/n$. But $n_0K=c$, and $nK=c\pm\tau$, so that $\sqrt{(g_0/g)}=c/(c\pm\tau)$, whence

$$\tau=\pm\{\sqrt{(g/g_0)}-1\}c. \tag{9}$$

Since this equation is a function of $\tau$, $g$, and $c$ as variables, it may be solved explicitly also for $c$ or $g$.

As physics students keeping in mind the *physical* meanings of the symbols, we can state problems accordingly. We have

$$c=\pm\tau/\{\sqrt{(g/g_0)}-1\}, \tag{9a}$$

and

$$g=(\tau/c\pm1)^2g_0. \tag{9b}$$

With $\tau=1$ sec, $c=86\,400$ sec, we get $g/g_0=(0.000\,011\,574\pm1.000\,000\,000)^2g_0$. The percentage change in $g$ is $100(g-g_0)/g_0=100\tau(\tau/c\pm2)/c$, which approximates $\pm200\tau/c$. We remember that $\tau$ is being regarded as a positive number.

Next, consider the increments

$$(\Delta g)_1\equiv\tau(\tau/c+2)g_0/c,$$

and

$$(\Delta g)_2\equiv\tau(\tau/c-2)g_0/c.$$

Then the ratio of these increments, $(\Delta g)_1/(\Delta g)_2=(\tau+2c)/(\tau-2c)\neq1$, corresponding to Eq. (6), where g is constant and the temperature variable. The percentage difference of this ratio from unity is $100\{[(\Delta g)_1/(\Delta g)_2]-1\}/1=400c/(\tau-2c)$, corresponding to Eq. (8*a*).

### BOTH TEMPERATURE AND $g$ VARIABLE

Students may be asked to derive the more general expression where the pendulum is uncompensated for temperature change and both the temperature and the altitude are variable. Now,

$$T/T_0=[(L_0/L)(g/g_0)]^{\frac{1}{2}},$$

and since $L=L_0(1+\alpha\Delta t)$, we have

$$T/T_0=\{g/[(1+\alpha\Delta t)g_0]\}^{\frac{1}{2}}.$$

But $n_0K=c$, and $nK=c+\tau$, while $n_0K\equiv n_0T_0=nT=c$, so that $T/T_0=n_0/n=c/(c\pm\tau)$, as before. If we eliminate $T/T_0$,

$$\tau=\pm c\{[(1+\alpha\Delta t)g_0/g]^{-\frac{1}{2}}-1\}, \tag{10}$$

which is a function of $\tau$, $c$, $\Delta t$, and g as variables Eq. (10) can be solved for any of the other three variables, and corresponding problems stated. Since $g=g_0+(\Delta g)$, the ratio $g_0/g$ in Eq. (10) can be replaced by the ratio $1/\{1+[(\Delta g)/g_0]\}$, and we can solve for the relative change in $g$, that is $(\Delta g)/g_0$, to be expected where any particular numerical values of $\tau$, $c$, and $\Delta t$, the temperature change from standard, are specified. Thus, Eq. (10) offers still more opportunity for *physical* exploration, guided by *algebraic* exploration. This can be much more than a matter of academic curiosity. It is a sort of exploration that historically has contributed to practical knowledge.

### CONCLUSION

Ours is a day of electrical clocks, synchronized with a master timekeeper. As long as their power supply remains uninterrupted, we do not worry about their correctness. But pendulum clocks are still being operated, represented frequently by family heirlooms or just antiques typified by the grandfather's clock. Also, clocks with seconds pendulums are to be found in physics laboratories. But in spite of their being somewhat outdated, pendulum clocks, especially those uncompensated for temperature changes, continue to demonstrate effectively physics principles that will always be with us. Such a clock performs faithfully, controlled by mechanical and thermal principles. Whether or not it keeps time, as we say, its behavior is neither abnormal nor "incorrect," for in fact it announces, accurately, both the number of times it has vibrated during the elapsed day, and the actual elapsed time in its indicated 86 400 sec. The error is on the part of the observer, who mistakes the indicated time for the actual time.

# Discovery of the Differential Thermometer*

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(Received April 30, 1953)

The differential thermometer was simultaneously discovered by Sir John Leslie and Count Rumford. The priority controversy between these two men is presented. Some years later Sir Humphry Davy depreciated Leslie's claim to the discovery. The ensuing debates cast interesting light on the personalities of the protagonists.

WHEN two scientists working in different places on similar problems manage almost simultaneously to invent similar new devices of obvious significance, a storm is sure to follow. The history of invention and of inventors is enlivened by several spectacular priority controversies which have never been settled because both claimants seem to deserve full credit.

Since the discovery is more important to the advance of knowledge than the name of the discoverer, a priority struggle of 150 years ago is interesting mostly as a comedy of manners, however inconvenient a biographer may find it. No physicist really cares today whether the differential thermometer was invented by Sir John Leslie or Count Rumford, or whether Sir Humphry Davy did justice to Leslie in a subsequent argument, but the story of the dispute provides amusing glimpses of famous personalities of the time. One concludes that, however great the progress of science, human nature has not been changing very much.

The debate over who first produced the differential thermometer continues today, although the heat of battle has long since died away. On the European continent, Rumford is given the credit with no mention of Leslie, but English and American historians of science consider Leslie the inventor, with no reference to Rumford. Professor E. C. Watson[1] follows this tradition in a recent edition of his "Reproductions of Prints, Drawings, and Paintings of Interest in the History of Physics," mentioning Leslie as famous for his invention of the instrument.

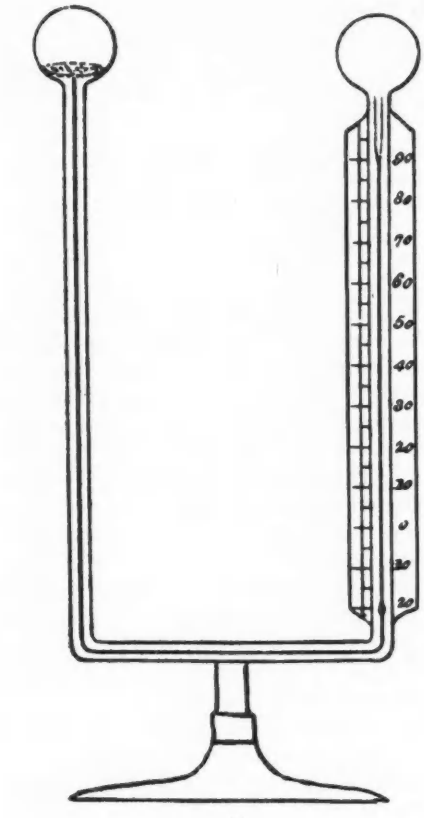
As to the facts in the case, Leslie in Scotland and Rumford in Bavaria not only invented similar thermometers at the same time, but designed them to carry out almost identical experiments on the radiation from reflecting and absorbing surfaces. So nearly identical were their investigations that immediate accusations of plagiarism were leveled against both men from various quarters. (Actually Leslie's "differential thermometer" and Rumford's "thermoscope" were not precisely identical, as Fig. 1 will show. Leslie's device had a long liquid column separating the air bulbs, while Rumford's had only a small bubble of liquid running in a horizontal section of tube.)

Count Rumford gives us a very detailed account of his side of the story:[2]

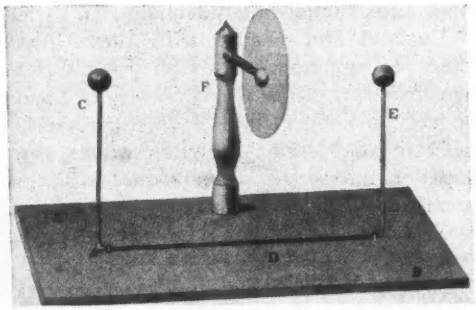
"I performed these experiments in Munich, in 1803, during the months of January, February, and March. According as the results seemed of importance, I immediately acquainted my friends in England and France with them. Among others, I communicated to Sir Joseph Banks, then President of the Royal Society of London, the very striking results of an experiment, on the 11th of March . . . with various vessels *blackened* and *covered with repeated coatings of varnish*, and I announced the results obtained. I also informed him of the discovery . . . of my *thermoscope*.

"Since Sir Joseph showed my letters to various persons, and since I did not keep my experiments or their results secret from him or from anyone else, my discovery was publicly mentioned in London even as early as the spring of the past year [1803]. As an incontrovertible proof of this fact, I can bring forward a letter from a

* Supported in part by a grant from the Penrose Fund of the American Philosophical Society.
[1] E. C. Watson, Am. J. Phys. **21**, 107 (1953).
[2] *The Works of Rumford* (American Acadamy of Arts and Sciences, Boston, 1873), Vol. II, p. 188.



(a)




(b)

FIG. 1. (a) Leslie's differential thermometer. (b) Rumford's thermoscope.

friend of mine . . . in which he congratulates me on the success of my researches, and informed me at the same time that he had learned what he knew with regard to my discoveries from Mr. Davy, a Professor at the Royal Institution, who had spoken publicly of them in his lectures on chemistry.

"The 6th of June there were sent to me from London . . . a letter from Mr. Davy . . . in which he informed me that Mr. Leslie had, a short time previously, published a memoir on heat, and that in it had described various experiments which bore a resemblance to some which I had performed.

"As I had, only a short time before, occupied the attention of the National Institute with an account of my recent researches and discoveries, the appearance of a book coming from England, and containing a description of a number of experiments and discoveries in many respects not dissimilar to my own, could not fail to create a certain feeling of surprise among the philosophers of Paris, as I could plainly enough perceive. . . .

"I am far from intending to assert that Mr. Leslie had any knowledge of those experiments of mine which bore a resemblance to those which he announced publicly in print. It is, however, equally certain that I did not know, and could not have known, the least thing about his . . . .

"As regards the *priority of the public announcement* of our discoveries, this point can be easily made clear by the statement of certain facts which do not admit of doubt.

"It is true that I cannot determine with any great accuracy the time when Mr. Leslie's book first saw the light; it cannot, however, possibly have been published before the middle of May of this year, for the dedication is dated at Largo, in Fifeshire (Scotland), the 20th of May, 1804. This would be, consequently, nearly a year after the time when the most remarkable results of my investigations were known in London."

Rumford's published proof that he could not have designed his experiments after Leslie's did not, however, still the clamor of accusations. In fact it reached proportions that even ladies of fashionable society entered the fray. We find the widow of the celebrated chemist Lavoisier writing to the Swiss physicist Pictet,[3] in June 1805:

[3] Unpublished letter, transcript in the collection of the American Academy of Arts and Sciences, Boston.

"I presume, Sir, that you have received the *Monthly Review* for the months of March and April, and that you have noted the manner in which Count Rumford is treated by this publication . . . . Your friendship for Count Rumford will certainly revolt at reading such an article; and don't you think it proper for you to come to his defense . . . . I am expressing to you, Sir, my idea and my desire to see an atrocious calamity repulsed . . . injustice pains true men, and you were certainly not in need of my warning to make you come to the Count's aid."[4]

Active interest in the controversy gradually died with the general acceptance in England of Leslie as the discoverer of the differential thermometer, while on the Continent Rumford was given the credit. However, the whole debate was reopened when Sir Humphry Davy published his *Elements of Chemical Philosophy* in 1812. The issues of the new controversy can best be described by Leslie himself:[5]

"In glancing over Davy's *Elements of Chemical Philosophy*, I was surprised to find it alleged that Van Helmont had given a sketch of a 'curious instrument, very similar to the differential thermometer;' and a few pages further on, to meet with this bottom note—'Plate I. Fig. [2a] represents Mr. Leslie's differential thermometer. Fig. [2b] is copied from Van Helmont. This instrument appears to have been the first in which the expansive power of heated air was exhibited by its action upon cold air.' On turning to this plate, I observe a very clumsy and distorted representation of my differential thermometer, placed by the side of another figure, bearing a general resemblance to it, and purporting to be a copy of Van Helmont's sketch. I soon perceived, however, that Van Helmont's description and figure [see Fig. 3] were essentially different from the representation which Sir Humphry has taken the trouble to give. In fact, the "curious instrument" described by the alchemist is no other than the common air-thermometer of Sanctorio or Drebbel[6] [see Fig. 4], invented more than forty years before his

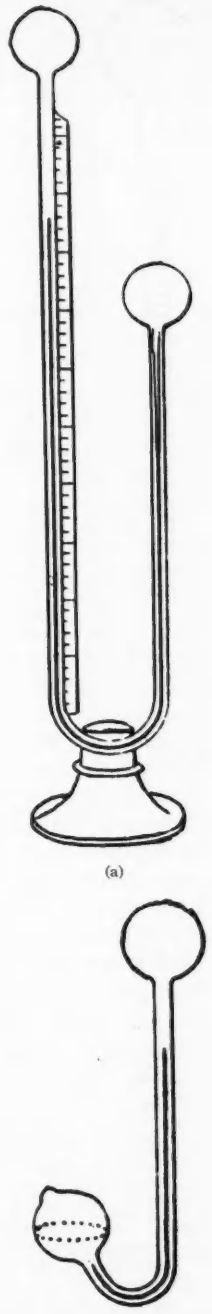



FIG. 2. (a) Davy's copy of Leslie's differential thermometer. (b) Davy's copy of Van Helmont's thermometer.

[4] Since Mme. Lavoisier married Rumford four months later, she may have had a more than casual interest in the "atrocious calamity" which was befalling him.

[5] J. Leslie, Phil. Mag. 4, 236 (1812).

[6] Boerhaave, *Elementa Cheminae*, Paris (1733) p. 83.

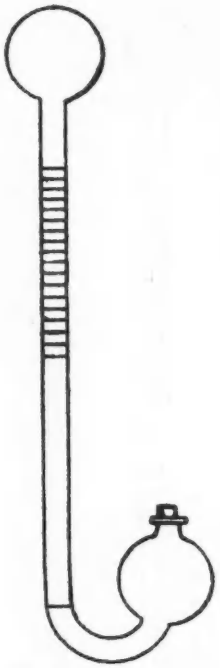


FIG. 3. (a) Leslie's copy of Van Helmont's thermometer.

death; only, for the sake of easier carriage, shaped like a siphon, the lower end being bent upwards, and terminating in a spherical cup, with a *small orifice*—one of the forms which it had from its earliest introduction. A learned person of the name of Heer imagining, it seems, as Sir Humphry has since done, that the instrument was absolutely closed, had proceeded to admire the perpetual motion of the contained liquid . . . To this Van Helmont replied, that the action of the machine no more produced perpetual motion than the changing of a weather-cock . . . he calls his rival, in the uncourtly language of those times, "an idiot," and charges him with "stupidity," for not perceiving that the instrument had an *aperture*, only slightly shut with a stopper, and not hermetically sealed, as it is most incorrectly figured in the *Elements of Chemical Philosophy*.

"I will not suppose that Sir Humphry intentionally misrepresented the meaning of Van Helmont; but then it follows, that either he had not read the passage to which he refers, or must have satisfied himself with a very superficial and careless inspection. This precipitancy is the more to be lamented, as it may possibly beget suspicion of want of accuracy or fairness in other matters of higher consequence."

Following this original complaint of Leslie against Davy, the *Philosophical Magazine* for 1812 and 1813 contains several articles on both sides of this argument. Both Sir John and Sir

FIG. 4. Drebbel's air thermometer (reference 6).

Humphry were accused of falsifying illustrations, suppressing facts, and wilful misrepresentations![7]

Controversies of this sort are interesting not so much for the physics involved as for the light they shed on the physicists. Sir John Leslie was involved in many such battles, and the sarcastic

[7] See, for example, "A.B." Phil. Mag. **40**, 329 (1812) and "C.D." Phil. Mag. **41**, 31 (1813).

insinuation for which he was noted is well illustrated in the passage quoted above. Count Rumford displayed further his egotistical personality during the first dispute when he wrote[2]:

"The *priority* in question, considered in and by itself, is of such slight importance that I should not have mentioned it at all, were it not that the facts which go to establish it tend at the same time to strengthen a far more important assertion, namely, that I am actually the *discoverer* of what I announced as discoveries."

## Normal Coordinates

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A technique for presenting the concept of normal coordinates to the beginning student of mathematical physics is described. The method differs but slightly from that found in standard textbooks on mathematical physics. This slight difference has been found to be of great assistance to students who are encountering normal coordinates for the first time.

NORMAL coordinates greatly facilitate the description of many-particle systems, provided these particles interact through linear restoring forces. Description of a system of $n$ degrees of freedom demands knowledge of the behavior of $n$ independent coordinates with time. These $n$ coordinates will in turn be solutions of $n$ simultaneous equations of motion. In general these equations of motion will be coupled due to the interaction forces and hence their solution becomes difficult. However, it can be shown[1,2] that there is one set of coordinates, namely the normal coordinates, in terms of which the $n$ equations of motion separate into a new set of $n$ independent equations which allow immediate solution.

Since many problems in modern physics involve systems of interacting particles, normal coordinates find rather widespread application. The interpretation of molecular spectra in terms of normal modes of vibration and their corresponding angular frequencies is one such application.[3] In the case of a quantum-mechanical system of several particles with linear mutual interactions it is found that Schrödinger's equation for the system separates into $n$ independent equations provided normal coordinates are used.[4] Some electrical circuits also allow the use of normal current or charge coordinates for solving the corresponding Kirchhoff equations.[5]

Normal coordinates are usually encountered for the first time by students in a senior or graduate course in mathematical physics. A technique for presenting this topic which differs slightly from that used in current standard textbooks[1,2] has been found helpful during a recent senior course offered by the author. The adoption of this technique followed an observation that mathematical detail seemed to obscure some important properties of normal coordinates for the beginning student. It was found that the slight change in *modus operandi* described below clarified these properties for the students. The mathematics, while exactly the same as for the usual approach, arises in a more direct fashion. The imperfections in rigor of the method are no more serious than those found in the conventional approach.

### 1. PROPERTIES OF NORMAL COORDINATES

Consider two identical oscillators describable by the two general coordinates[6] $q_1$ and $q_2$. If

[1] J. C. Slater and N. H. Frank, *Mechanics* (McGraw-Hill Book Company, Inc., New York, 1947), first edition, p. 122.
[2] R. B. Lindsay, *Concepts and Methods of Theoretical Physics* (D. Van Nostrand Company, Inc., New York, 1951), first edition, p. 95.
[3] G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., New York, 1945), first edition, p. 61.
[4] J. C. Slater, *Quantum Theory of Matter* (McGraw-Hill Book Company, Inc., New York, 1951), first edition, p. 313.
[5] L. A. Pipes, *Applied Mathematics for Engineers and Physicists* (McGraw-Hill Book Company, Inc., New York, 1946), first edition, p. 172.
[6] These coordinates are not restricted to linear displacements; they may be angles, for example.

these two oscillators are coupled in some manner[7] with a coupling coefficient $k_{12}$, the resulting system will be governed by the two equations of motion

$$\ddot{q}_1+kq_1+k_{12}q_2=0, \tag{1}$$

$$\ddot{q}_2+kq_2+k_{12}q_1=0. \tag{2}$$

Addition of Eqs. (1) and (2), or subtraction of the two, leads, respectively, to two different equations,

$$(\ddot{q}_1+\ddot{q}_2)+(k+k_{12})(q_1+q_2)=0, \tag{3}$$

$$(\ddot{q}_1-\ddot{q}_2)+(k-k_{12})(q_1-q_2)=0, \tag{4}$$

which, of course, are equivalent to the original equations. From Eq. (3) it is seen that the combination of coordinates $q_1+q_2=Q_1$ oscillates (if $k+k_{12}>0$) with an angular frequency $\Omega_1=(k+k_{12})^{\frac{1}{2}}$, while from Eq. (4) it is seen that the combination of coordinates $q_1-q_2=Q_2$ oscillates (if $k-k_{12}>0$) with an angular frequency $\Omega_2=(k-k_{12})^{\frac{1}{2}}$. When written in terms of $Q_1$ and $Q_2$, Eqs. (1) and (2) separate and appear as two independent equations,

$$\ddot{Q}_i+\Omega_i^2Q_i=0, \quad i=1, 2. \tag{5}$$

The coordinates $Q_i$ are usually referred to as normal coordinates, and the angular frequencies $\Omega_i$ as normal frequencies. It can be shown[8] that the total energy of the system, when expressed as a function of the $Q_i$'s and their derivatives, contains only squared terms, no mixed products. These facts then serve as the identifying characteristics of normal coordinates:

(1) In terms of normal coordinates the equations of motion for coupled oscillators separate into independent equations, each of which contains only one of the normal coordinates as an unknown.

(2) Each normal coordinate oscillates with a characteristic normal frequency.

(3) The energy of the oscillating system can be expressed as a combination of the squares of the $Q_i$'s and their derivatives.

The question immediately arises as to the possibility of determining normal coordinates for the general vibrating system of $n$ degrees of freedom. This generalization is discussed in Part 2.

[7] They may be coupled by a spring if they are mass points, by a mutual inductance if they are circuits, etc.

[8] Reference 1, p. 133.

## 2. SYSTEMS OF $n$ DEGREES OF FREEDOM

So far our discussion has progressed along customary lines. It is in the generalization of the concept to more complicated systems that the modification is made. A system of $n$ degrees of freedom will be governed by $n$ equations of the form[9]

$$\ddot{q}_i+\sum_j k_{ij}q_j=0 \quad i=1, 2, \cdots n. \tag{6}$$

The summation in Eq. (6) extends from $j=1$ through $j=n$. All subsequent summations will be understood to have the same limits unless otherwise specified. Similarly, all subscripts will be assumed to have a range from 1 through $n$ unless otherwise specified.

### 2.1. Conventional Solution

The standard procedure for solving Eqs. (6) is to assume *a priori* that each $q_i$ will oscillate with some undetermined angular frequency $\Omega$ and substitute $q_i=A_i\cos(\Omega t+\phi_i)$ into the equations of motion where $A_i$ and $\phi_i$ are constant. This results in the $n$ equations

$$\sum_j k_{ij}A_j-\Omega^2A_i=0. \tag{7}$$

In order that these equations be solvable for the $A_i$'s the secular determinant

$$|k_{ij}-\Omega^2\delta_{ij}| \tag{8}$$

must be made to vanish, where $\delta_{ij}$ is the Kronecker symbol. This restricts $\Omega^2$ to one of the $n$ roots of the determinant. These $\Omega$'s are the $n$ normal frequencies of oscillation. For each different value of $\Omega$ it is possible to determine the ratios of the $A_i$'s from Eq. (7). The solutions are then written as

$$q_i=\sum_j r_{ij}B_j\cos(\Omega_j t+\phi_j), \tag{9}$$

where $r_{ij}B_j$ is the value of $A_i$ when $\Omega=\Omega_j$. The ratios of the $r_{ij}$'s are determined from Eq. (7) with $\Omega=\Omega_j$, and their magnitudes may be fixed by an arbitrary normalization condition such as

[9] A more general form would be $\Sigma_j(a_{ij}\ddot{q}_j+k_{ij}q_j)=0$. This can be reduced to Eq. (6) by solving the $n$ equations for the $\ddot{q}_i$'s in terms of the $q_i$.

$\sum_i (r_{ij})^2=1$. It can be shown that the $r_{ij}$'s then satisfy the orthogonality condition

$$\sum_i r_{ij}r_{im}=\delta_{jm}. \tag{10}$$

If Eq. (9) is multiplied by $r_{im}$, the result summed over $i$, and condition (10) applied to the sum, the result is

$$\sum_i r_{im}q_i=B_m\cos(\Omega_m t+\phi_m). \tag{11}$$

Thus, the combination $\sum_i r_{im}q_i$ oscillates with the normal frequency $\Omega_m$. The $m$th normal coordinate then is

$$Q_m=\sum_i r_{im}q_i. \tag{12}$$

### 2.2. Modified Solution

If the normal coordinates of the general system described by Eqs. (6) are of primary interest, a slightly different approach to the solution is more convenient. It will develop that the modified method will also eliminate the necessity for the *a priori* assumption that the system of oscillators will oscillate rather than experience a decay.

A normal coordinate $Q$ will satisfy an equation similar to Eq. (5) and will also be some linear combination of the $q_i$'s. Let us define $Q$ to be $\sum_i c_iq_i$. A differential equation for $Q$ can be obtained if the $i$th equation in the set given by Eq. (6) is multiplied by some constant $c_i$ and the resulting equations summed over $i$. The equation takes the form

$$\ddot{Q}+\sum_i c_i\sum_j k_{ij}q_j=0. \tag{13}$$

If Eq. (13) is to describe the motion of a normal coordinate, i.e., in order for $Q$ to be a normal coordinate of the motion, the coefficients $c_i$ must satisfy the relations

$$\sum_i c_i\sum_j k_{ij}q_j=\Omega^2\sum_i c_iq_i. \tag{14}$$

In an expanded form these equations are

$$\begin{aligned}
(k_{11}-\Omega^2)c_1+k_{21}c_2+\cdots+k_{n1}c_n&=0\\
k_{12}c_1+(k_{22}-\Omega^2)c_2\cdots+k_{n2}c_n&=0\\
\cdot\quad\quad\cdot\quad\quad\cdot&\\
\cdot\quad\quad\cdot\quad\quad\cdot&\\
\cdot\quad\quad\cdot\quad\quad\cdot&\\
k_{1n}c_1+k_{2n}c_2+\cdots+(k_{nn}-\Omega^2)c_n&=0.
\end{aligned} \tag{15}$$

In order that the equations in (15) yield nontrivial solutions for the $c_i$'s, the secular determinant of the coefficients must vanish. This is the same determinant as that shown in Eq. (8) and will lead to the same $n$ values of $\Omega$ for the normal frequencies. For each value $\Omega_m$, Eqs. (15) will allow solution for the ratios of the $c_i$'s. Let us denote by $\gamma_{im}$ the value of $c_i$ when $\Omega=\Omega_m$. If the equations in (15) are used together with an arbitrary normalization condition $\sum_i \gamma_{im}^2=1$, all the constants will be determined. In this case the $m$th normal coordinate $Q_m$ will become

$$Q_m=\sum_i \gamma_{im}q_i. \tag{16}$$

The $Q_m$'s determined from Eq. (16) can differ from those determined from Eq. (12) by a constant multiplicative factor at most. Since $Q_m$ satisfies the equation $\ddot{Q}_m+\Omega_m^2Q_m=0$, it follows that

$$Q_m=C_m\cos(\Omega_m t+\phi_m). \tag{17}$$

## 3. DISCUSSION

From the preceding section it is obvious that little difference in mathematical difficulty exists between the two methods. If major emphasis is to be placed on the solution for the $n$ $q_i$'s, the conventional approach is preferable, since it leads immediately to a solution for the $q_i$'s—the normal coordinates are obtained only incidentally and at the expense of an additional operation. On the other hand, if the normal coordinates are of primary interest, the second method leads to them directly—the $q_i$'s can be obtained only after an additional operation.

Apparently, it is this distinction which leads to the students' preference for the latter method. The elimination of the *a priori* assumption of an oscillatory solution also appeals to students who are considering such systems for the first time. In addition the second method eliminates the objection that the defining properties of normal coordinates are not used in the standard solution.

Perhaps others have used this direct approach to normal coordinates prior to this time. In any event the author will welcome any comments as regards the relative merit of the two approaches.

# Some Current Misinterpretations of N. L. Sadi Carnot's Memoir and Cycle*

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The indiscriminate translation of the words "feu," "chaleur," and "calorique," uniformly as heat (or wärme) in the accepted translations of Carnot's memoir, without recognizing differences in meaning which Carnot consistently implied, has led to erroneous misinterpretations of his thesis, which are prevalent in present day texts.

Carnot had at least an intuitive conception of the modern interpretation of entropy in his consistent use of "chute de calorique" as analogous to "chute d'eau." He never speaks of "chute de chaleur."

One needs only to identify "calorique" as entropy and "chaleur" as heat to achieve simplicity and lucidity in understanding his memoir and at the same time imparting accordance with modern theory for pertinent passages that have been misconstrued.

IT has been said that it takes five years to get a new idea into the textbooks, and if it is wrong, it takes twenty-five years to get it out. Nothing seems to perpetuate itself so effectively as a misconception, particularly when it offers an apparently simple explanation of an abstract subject and has been advocated over a long period of time.

There are three misconceptions which still persist in many of our latest and best textbooks, one century after the fundamental error was made by Clapeyron (1834),[1] and one third of a century after his error was pointed out by Callendar.[2] They may be summarized as follows:

(1) Carnot[3] obtained a valid result, but he did so by employing an erroneous theory of heat; namely, the now discredited substantive or so-called caloric theory of heat;

(2) that Carnot discovered the second law of thermodynamics without recognizing or appreciating the importance and necessity of the first law;

(3) that Carnot's analogy, that the descent of "heat?" (chute de calorique) through a reversible engine for the production of motive power could be likened to the descent of water (chute d'eau) through a mill, represents an incorrect conception in that it leads to contradictions with the first law and, consequently, makes Carnot's proof invalid.

The primary purpose of this paper is to analyze the historical origin and development of these misconceptions for a better understanding of the fallacies in the hope that the reader will then become more receptive towards what, I believe, represents a simple, self-consistent, and rational presentation of Carnot's principle.

It is of little moment today whether or not Carnot was incorrectly interpreted and unjustly represented by his followers. What really matters is that our textbooks of the future should give the clearest and simplest interpretation of his fundamental principle consistent with the known facts.

I assert that these three misconceptions vanish and the presentation becomes simple and understandable when one reads the original, abandons the gratuitous and erroneous notion that Carnot was employing the discredited substantive or caloric theory of heat when he used the term "calorique," and, finally, interprets the term "calorique" as "entropy." This interpretation of "calorique" makes Carnot a modern writer. It removes any question of his treatment violating the first law, as was claimed by Kelvin.

That Carnot's "calorique" should be interpreted today as "entropy" was first pointed out in 1937 by Brønsted[4] in a memoir which quite

* Read at the American Physical Society, January 29, 1949. Brief Abstract, Science 109, 598 (June 10, 1949).

[1] Clapeyron, J. de l'ac polytechn. 14, 23, Cahier 153 (1834).

[2] H. S. Callendar, article on "Heat," *Encyclopedia Britannica*, 1911 and later editions.

[3] N. L. Sadi Carnot, *Réflections sur la puissance motrice du feu* (Bachelier, Paris, 1824); (Reimpression Paris, 1878) see: Compt. rend. 87, 967 (1878). Biographie et manuscrits (l'Academie des Sciences, Gauthier-Villars, Paris, 1927).

[4] J. N. Brønsted, "OM Relationen Mellem Varme og Arbeide," Kgl. Danske Videnskab. Selskab., Math-fys. Medd. XV, No. 4 (1937), p. 58 (unpublished translation by C. V. King).

understandably has escaped the attention it deserves since it was published in Danish. He says:

"Of the earlier authors, Carnot really approached this (Brønsted's) viewpoint most closely. Ostwald[5] has with reason remarked that the designation 'calorique' which is usually identified with 'heat material' (*wärmestoff*) was consistently used by Carnot, where the mechanical energy of heat is compared with the mechanical energy of a waterfall, while for more general considerations, he uses the word 'chaleur.' This circumstance might indicate a purely intuitive conception of an essential difference in these thermal designations. There is apparently required only an exchange of the concept 'entropy' for the concept 'calorique' for the Carnot treatment to attain complete fundamental agreement with the present representations.

"Whether the considerations concerning the mechanical equivalent of heat in Carnot's posthumous diary indicated a change in his original conception of the heat engine's doctrine, cannot be ascertained here."

These statements of Brønsted have furnished the inspiration for the present investigation; namely, to re-examine the memoir along with the translations and interpretations that have been made of it. The study has been most enlightening.

In the first place, the original is difficult of access with the result that present day textbook writers unknowingly perpetuate erroneous interpretations of scientists who, despite their eminence, were unable to consult the original work. For example, Clausius,[6] in the opening footnote of his classic monograph, states:

"I have not been able to obtain a copy of this book and am acquainted with it only through the work of Clapeyron and Thompson, from the latter of whom are quoted the extracts afterwards given" (translation by Magie).[7]

That certainly before his death in 1832 Carnot believed in the mechanical theory of heat and not in the substantive theory is recognized today by all who have taken the trouble to read his posthumous notes.[8] These notes appear as Appendix A in the translation by Thurston[8] and are given later. They shed much light upon the scientific penetration of the man and the clarity of his thoughts. Carnot's familiarity with the previous work of Davy, Rumford, and others, and his proposals for new experiments to demonstrate the validity of the mechanical theory, certainly establish that his grasp and understanding of this problem exceed that of many illustrious investigators of the next quarter century.

The following passage taken from the original memoir should be sufficient evidence that even in 1824 Carnot was advocating the mechanical theory of heat and appreciated the implications of the *first* law (translation by Magie,[7] p. 12):

"The objection will perhaps here be made that perpetual motion has only been demonstrated to be impossible in the case of mechanical actions, and that it may not be so when we employ the agency of heat or of electricity; *but can we conceive of the phenomena of heat and of electricity as due to any other cause than some motion of bodies*, and, as such, *should they not be subject to the general law of mechanics?* Besides, do we not know *a posteriori* that all the attempts made to produce perpetual motion by any means whatever have been fruitless; that no truly perpetual motion has ever been produced, meaning by that, a motion which continues indefinitely without change in the body used as an agent?

"The electromotive apparatus (Volta's pile) has sometimes been considered capable of producing perpetual motion; the attempt has been made to realize it by the construction of the dry pile, which is claimed to be unalterable; but, in spite of all that has been done, the apparatus always deteriorates perceptibly when its action is sustained for some time with any energy.

[5] Ostwald, *Klassiker der exacten Wissenschaften* (Englemann, Leipzig, 1892), Nr. 37.

[6] Clausius, *Abhandlungen über die mechanische Wärmetheorie* (Braunschweig, Vieweg, 1864 and later editions).

[7] Magie, *The Second Law of Thermodynamics* (American Book Company, New York, 1899), p. 65.

[8] R. H. Thurston, Translation from original French of N. L. S. Carnot's *Reflections on the Motive Power of Heat* (John Wiley and Sons, Inc., New York, 1897), second edition.

"The general and philosophical acceptation of the words *perpetual motion* should comprehend not only a motion capable of indefinite continuance after it has been started, but also the action of an apparatus, of a set of bodies, capable of creating motive power in an unlimited quantity, and of setting in motion successively all the bodies of nature, if they are originally at rest, and of destroying in them the principle of inertia, and finally capable of furnishing in itself all the forces necessary to move the entire universe, to prolong and to constantly accelerate its motion. Such would be a real creation of motive power. *If this were possible, it would be useless to search for motive power in combustibles*, in currents of water and air. We should have at our disposal an inexhaustible source from which we could draw at will."

Since the posthumous notes have been available since 1878, it is difficult to understand how Magie could add the following editorial footnote, p. 7:

"Caloric is heat considered as an indestructible substance. The word is used by Carnot interchangeably with feu, fire or heat."

Any lingering doubt that Carnot was using feu, calorique, and chaleur indiscriminately, however, should be dispelled by the following translation from Thurston,[8] p. 217, 219–222:

"II. Notes of Sadi Carnot on Mathematics, Physics and Other Subjects (1824–32).

"When a hypothesis no longer suffices to explain phenomena, it should be abandoned.

"This is the case with the hypothesis which regards caloric as matter, as a subtile fluid.

"The experimental facts tending to destroy this theory are as follows:

"(1) The development of heat by percussion or the friction of bodies (experiments of Rumford, friction of wheels on their spindles, on the axles, experiments to be made). Here the elevation of temperature takes place at the same time in the body rubbing and the body rubbed. Moreover, they do not change perceptibly in form or nature (to be proved). *Thus heat is produced by motion. If it is matter, it must be admitted that the matter is created by motion.*

"(2) When an air pump is worked, and at the same time air is admitted into the receiver, the temperature remains constant in the receiver. It remains constant on the outside. Consequently, the air compressed by the pumps must rise in temperature above the air outside, and it is expelled at a higher temperature. The air enters then at a temperature of 10°, for instance, and leaves at another, 10°+90° or 100°, for example. *Thus heat has been created by motion.*

"(3) If the air in a reservoir is compressed, and at the same time allowed to escape through a little opening, there is by the compression elevation of temperature, by the escape lowering of temperature (according to Gay-Lussac and Welter). The air then enters at one side of one temperature and escapes at the other side at a higher temperature, from which following the same conclusion as in the preceding case.

"(Experiment to be made: To fit to a high-pressure boiler a cock and a tube leading to it and emptying into the atmosphere; to open the cock a little way, and present a thermometer to the outlet of the steam; to see if it remains at 100° or more; to see if steam is liquefied in the pipe; to see whether it comes out cloudy or transparent.)

"(4) The elevation of temperature which takes place at the time of the entrance of the air into the vacuum, an elevation that cannot be attributed to the compression of the air remaining (air which may be replaced by steam), can therefore be attributed only to the friction of the air against the walls of the opening, or against the interior of the receiver, or against itself.

"(5) M. Gay-Lussac showed (it is said) that if two receivers were put in communication with each other, the one a vacuum, the other full of air, the temperature would rise in one as much as it would fall in the other. If, then, both be compressed one half, the first would return to its previous temperature and the second to a much higher one. Mixing them, the whole mass would be heated.

"When the air enters a vacuum, its passage through one small opening and the motion imparted to it in the interior appear to produce elevation of temperature.

"We may be allowed to express here an hypothesis in regard to the nature of heat.

"At present, light is generally regarded as the result of a vibratory movement of the ethereal fluid. *Light produces heat*, or at least accompanies the radiating heat, and moves with the same velocity as heat. Radiating heat is then a vibratory movement. It would be ridiculous to suppose that it is an emission of matter while the light which accompanies it could be only a movement.

"*Could a motion (that of radiating heat) produce matter (caloric)?*

"*No, undoubtedly; it can only produce a motion. Heat is then the result of a motion.*

"Then it is plain that it could be produced by the consumption of motive power, and that it could produce this power.

"All the other phenomena—composition and decomposition of bodies, passage to the gaseous state, specific heat, equilibrium of heat, its more or less easy transmission, its constancy in experiments with the calorimeter—could be explained by this hypothesis. But it would be difficult to explain why, in the development of motive power by heat, a cold body is necessary; why, in consuming the heat of a warm body, motion cannot be produced."

Since these notes were given considerable publicity in 1878, it is also difficult to understand how Clausius,[6] in the edition of 1887, could write the following underscored sentence (footnote 2, p. 93):

"(2) Von einigen neueren Schriftstellern wird die Gleichung $(V)$ $(\int dQT=0)$ die Carnot'sche Gleichung genannt. Man kann aber mit Sicherheit annehmen, dass diese Schriftsteller das Carnot'sche Werk (Réflèxions sur la puissance motrice du feu, Paris, 1824) nicht kennen, denn aus diesem Werke ergiebt sich, dass Carnot diese Gleichung nicht aufgestellt hat, und nach seinen Ansichten über die Wärme auch gar nicht hat aufstellen können. *Da er nämlich die Wärme für einen Stoff hielt, dessen einmal bestehende Menge sich weder vermehren noch vermindern lässt*, so musste er, wie er es auch in der oben (S. 80) citierten Stelle bestimmt ausgesprochen hat, annehmen, dass die während eines Kreisprocesses von dem veränderlichen Körper abgegebenen Wärmemengen zusammen eben so gross seien, wie die aufgenommenen. Er konnte daher für einen Kreisprocess nur die Gleichung

$$\int dQ=0$$

aufstellen, welche mit der Gleichung $(V)$ unvereinbar ist."

In short, Clausius criticizes a contemporary writer for not reading Carnot's memoir. Either Clausius never read the original as late as 1887, or if he did, he did not understand it, for Carnot never said that $\int dQ=0$ when work is produced in his cycle. The author who has clearly pointed out the source of this error was the English physicist, H. S. Callendar.[2] Extracts from his article on *Heat* are now quoted in support of our thesis.

11th Edition (1911). p. 142 *et seq.* "Carnot's description of his cycle and statements of his principle have been given as nearly as possible in his own words, because some injustice has been done him by erroneous descriptions and statements."

14th Edition, p. 320. "Carnot's axiom—Carnot here, and throughout his reasoning makes a fundamental assumption, which he states as follows: 'When a body has undergone changes and after a number of transformations is brought back identically to its original state, considered relatively to density, temperature and mode of aggregation, it must contain the same quantity of heat (chaleur) as it contained originally.' *Clausius* (Pogg. Ann. 79, p. 369) *and others have misinterpreted this assumption* and have taken it to mean that the quantity of heat required to produce any given change of state is independent of the manner in which the change is effected *which Carnot does not here assume.* Heat, according to Carnot in the type of machine we are considering, can evidently be a cause of motive power only by virtue of changes of volume or form produced by alternate heating and cooling."

After discussing Carnot's temperature functions, Callendar writes, p. 322, "As Carnot himself remarks: 'The main principles on which the theory of heat rests require the most careful examination. Many experimental facts appear almost in-

explicable in the present state of this theory.' Carnot's work was subsequently put in a more complete analytical form by B. P. E. Clapeyron (J. de l'ac polytechn. 1834).

"Unfortunately, in describing Carnot's cycle, he (Clapeyron) assumed the caloric theory of heat, and made some unnecessary mistakes, *which Carnot, (who, we now know, was a believer in the mechanical theory) had been very careful to avoid.* Clapeyron directs one to compress the gas at the lower temperature in contact with the body B *until the heat disengaged is equal to that which has been absorbed at the higher temperature.* He (Clapeyron) assumes that the gas at this point contains the same quantity of heat as it contained in its original state at the higher temperature, and that, when the body B is removed, the gas will be restored to its original temperature, when compressed to its initial volume.

"*This mistake is still (erroneously) attributed to Carnot, and regarded as a fatal objection to his reasoning by many writers.* For example: Professor W. Thomson (Lord Kelvin in Phil. Mag. 1852) stated that 'Carnot's original demonstration utterly fails' and he accordingly introduced the 'corrections' attributed to James Thomson and Clerk Maxwell respectively. In reality, Carnot's original demonstration requires no correction."

p. 324. "In the second part of his paper Clausius (Pogg. Ann. 1850) introduced Carnot's principle, which he quotes as follows: 'The performance of work is equivalent to a transference of heat from a hot to a cold body without the quantity of heat being thereby diminished.'

"*This is quite different from Carnot's way of stating his principle,* and has the effect, of exaggerating the importance of Clapeyron's unnecessary assumption."

When the writer examined the original memoir, he was impressed by Carnot's almost perfect consistency in usage (noted by Ostwald and Brønsted) of three technical terms: feu, chaleur, and calorique.

Table I gives a summary of the translations or interpretations given these three terms by subsequent writers. The almost universal translation of "feu" as "heat" instead of fire or flame in the title is not important. However, it serves to emphasize the need for careful translation and interpretation when we proceed to the more subtle problem of the distinction between "chaleur" and "calorique."

TABLE I. Interpretation of Carnot's terms.

| Carnot (1824) | Kelvin (1849–52) | Clausius (1850) | Thurston (1890) Magie (1899) (translation) | Ostwald (1892) (translation) | Brønsted (1937) |
|---|---|---|---|---|---|
| feu<br>chaleur<br>calorique | heat | wärme | heat<br>heat<br>caloric | feuer<br>wärme<br>wärmestoff | (none given)<br>heat<br>entropy |

## BRØNSTED'S ENERGETICS

During the past decade, Brønsted[4,9–12] of Copenhagen has been engaged in a critical re-examination of the foundations and concepts of thermodynamics.

His researches are not only in harmony with the historical statements made by Callendar, but they lead to the further assertion that Clausius, in particular, in introducing the so-called "compensations" required in his form of statement of the second law has misconstrued and unnecessarily complicated Carnot's very simple and essentially correct interpretation of this cycle.

Brønsted has given this assertion as a special example in developing his system of energetics. Since his extensive publications on this subject have been largely in Danish, the writer[13] with Olav Foss and Howard Reiss have presented a resumé in English. In that paper, the complete equivalence of Brønsted's new principles with the two classical laws of thermodynamics is established. It is shown that his system possesses certain advantages over present presentations.

Brønsted calls his system "Energetics" because it is a broader term than thermodynamics and because it resurrects certain of the older ideas of Meyerhoffer, Helm, Mach, and Ostwald; namely, that all forms of energy may be considered as composed of an intensity and a con-

[9] J. N. Brønsted, Kgl. Danske Vidensk. Selskab., Mathfys. Medd. XVI, No. 10 (1939), and XIX, No. 8 (1941).
[10] J. N. Brønsted, Phil. Mag. (7) **29**, 449 (1940).
[11] J. N. Brønsted, J. Phys. Chem. **44**, 699 (1940).
[12] J. N. Brønsted, *Principer og Problemer i Energetiken* (Københavns Univ. Festskrift., Copenhagen, 1946).
[13] La Mer, Foss, and Reiss, Ann. N. Y. Acad. Sci. **51**, 605 (1949); Acta. Scand. **3**, 1238 (1949).

jugate capacity factor. Brønsted, however, recognized and carefully avoided the pitfalls which wrecked this older system of Energetics; consequently, his system is not to be confused with the Energetics of the decade 1890 to 1900.

Brønsted asserts that every work producing process requires the transport or movement of an extensive property through a conjugate difference of potential. These extensive properties are called quantities, and are so defined that they are conserved for reversible processes in an isolated system. Although immediately obvious for quantities such as mass, chemical substance, electric charge, etc., it is not so immediately obvious that the conservation principle must hold in all cases for quantities like volume or surface area. The reader is referred to the paper by La Mer, Foss, and Reiss[13] for proof.

When a quantity—like electric charge, mass, volume, entropy, etc.,—descends reversibly through a difference of potential, useful work or motive power becomes available for storage in a work reservoir. When the quantity descends irreversibly through the same difference of potential, no useful work can be stored in a work reservoir. The opportunity for doing work has been lost forever by the irreversible transport of the quantity. The principle of the conservation of energy embodied in the first law is maintained in the irreversible case by the production of an amount of heat equal to the "loss of work," or what amounts to the same thing, the production of an equivalent amount of entropy multiplied by the temperature at which the entropy is produced, i.e., $\delta Q'' = T\delta S''$ (double primes meaning a produced quantity as opposed to a transported quantity, single primes).

This means that "entropy" is unique among all of the quantities. In reversible processes it is transported unchanged, but in irreversible processes, it alone can be produced. Thus, an *irreversible thermal* process always entails not only the reversible transport of an invariant amount of entropy, but, in addition, a supplementary amount of entropy is created at progressively lower temperatures by the irreversible character of the process of heat conduction. This point will be treated in more detail later.

With this abbreviated presentation of *one* of Brønsted's new views, we return to our main topic. What did Carnot say and mean?

We now quote pertinent passages from Thurston's translation of Carnot's memoir and suggest that the reader interpret "caloric" as "entropy" and not as the discredited fluid of the substantive theory which Thurston as well as all other previous translators (Magie) and expositors (Clausius) have done.

Thurston, p. 44: "The production of motion in steam-engines is always accompanied by a circumstance on which we should fix our attention. This circumstance is the re-establishing of equilibrium in the caloric; that is, its passage from a body in which the temperature is more or less elevated, to another in which it is lower.

(p. 46) "The production of motive power is then due in steam-engines *not to an actual consumption of caloric, but to its transportation from a warm body to a cold body;* that is, to its re-establishment of equilibrium—an equilibrium considered as destroyed by any cause whatever, by chemical action such as combustion, or by any other. We shall see shortly that this principle is applicable to any machine set in motion by heat.

(p. 51) "*wherever there exists a difference of temperature, motive-power can be produced.* Reciprocally, wherever we can consume this power, it is possible to produce a difference of temperature, it is possible to occasion destruction of equilibrium in the caloric.

(pp. 49–50, and footnote) "It is natural to ask here this curious and important question: Is the motive power of heat invariable in quantity, or does it vary with the agent employed to realize it as the intermediary substance, selected as the subject of action of the heat?

"It is clear that this question can be asked only in regard to a given quantity of caloric,* *the difference of the temperatures also being given.*" (italics by V. K. L.)

(footnote) "*It is considered unnecessary to explain here what is quantity of caloric or quantity of heat (for we employ these two expressions indifferently), or to describe how we measure these quantities by the calorimeter. Nor will we explain what is meant by latent heat, degree of temperature, specific heat, etc.

The reader should be familiar with these terms through the study of the elementary treatises of physics or of chemistry.

(pp. 60–61 and footnote) "According to established principles at the present time, we can compare with sufficient accuracy the motive power of heat to that of a waterfall. Each has a maximum that we cannot exceed, whatever may be, on the one hand, the machine which is acted upon by the water, and whatever, on the other hand, the substance acted upon by the heat. The motive power of a waterfall depends on its height and on the quantity of the liquid; the motive power of heat depends also on the quantity of caloric used, and on what may be termed, on what in fact we will call, *the height of its fall*,* that is to say, the difference in temperature of the bodies between which the exchange of caloric is made. In the waterfall the motive power is exactly proportional to the difference of level between the higher and lower reservoirs. In the fall of caloric the motive power undoubtedly increases with the difference of temperature between the warm and the cold bodies; but we do not know whether it is proportional to this difference. We do not know, for example, whether the fall of caloric from 100 to 50 degrees furnishes more or less motive power than the fall of this same caloric from 50 to zero. It is a question which we propose to examine hereafter.

(footnote) "*The matter here dealt with being entirely new, we are obliged to employ expressions not in use as yet, and which perhaps are less clear than is desirable."

Carnot's footnote (bottom p. 50, Thurston translation) stating that it is considered unnecessary to explain what is quantity of "caloric or quantity of heat," has been used to support the view that Carnot was using "calorique" and "chaleur" indiscriminately. If we recognize that Carnot at least had in mind something like entropy when he spoke of "chute de calorique," since he never spoke of "chute de chaleur" in treating the motive power of flame (feu), but instead consistently restricted his use of the word "chaleur" to the general term we now call heat (symbol $Q$), it does seem that the issue ought no longer to be confused by Magie's and Thurston's footnotes, particularly in the light of Carnot's posthumous notes and the pertinent paragraphs just quoted.

Regardless of whether or not one cares to credit Carnot with the correct interpretation of the operation of the ideal heat engine, the writer contends that Brønsted has given a simpler exposition than Clausius and his presentation merits the attention of the textbook writers of the future.

To summarize matters, the operation of the Carnot engine can ke explained most simply as follows:

1. The engine absorbs reversibly an amount of heat $\delta Q_u$ from the upper temperature entropy reservoir $R_u$ at the constant temperature $T_u$. It is immaterial whether or not the quantity absorbed is designated as $\delta Q_u$ or $\delta S$, since at constant temperature they are related by the defining equation

$$\delta Q_u = T_u \delta S.$$

2. The engine rejects reversibly the same amount of entropy $\delta S$ but a different amount of heat $\delta Q_1$ at the constant temperature $T_1$ to the lower reservoir $R_1$, since

$$\delta Q_1 = T_1 \delta S,$$

but $T_1 < T_u$ and $\delta S_u = \delta S_1 = \delta S$ (a reversible process).

3. The first law demands that an amount of work $\delta A$ be delivered by the engine to a work reservoir equal to the difference (in proper units)

$$\delta A = Q_u - Q_1,$$

or what amounts to the same thing

$$\delta A = (T_u - T_1)\delta S;$$

namely, the descent (transport) of a constant amount of entropy $\delta S$ between two potential (temperature) levels. In other words, "chute de calorique" is exactly like "chute d'eau," in a water mill, except that "calorique" is not $Q$ as Kelvin and Clausius erroneously presumed Carnot had meant.

The above is purely a bookkeeping of energetic terms.

Classical thermodynamics has not always been content with this phenomenological description, but has looked for a genetic interpretation

from a more complicated standpoint. Whereas Brønsted's presentation views the process merely as a transport of entropy from the upper to the lower temperature, the total entropy of the system and surroundings remaining constant as it must in a reversible process, the traditional view of Clausius, consists in the transformation of an amount of heat $(Q_u - Q_1)$ into work, this quantity of heat being taken from the reservoir $R_u$ along with a supplementary transport of heat $Q_1$ which falls from $R_u$ to $R_1$. Thus, in addition to the heat-work transformation, a parallel heat transport takes place which is regarded as a compensation for the main process. This compensation explanation is unnecessary.

There remains only the matter of interpreting the efficiency $\eta$. The technical problem of producing work thermally consists even with an ideally functioning mechanism not in the procurement once for all of heat reservoirs at different temperatures, but in the maintenance of the necessary temperature state in the reservoirs while the system operates continuously. Introduction of entropy (or heat) to the high-temperature reservoir can be designated the first of the operations unavoidably necessary in maintaining a steady state of work production, and the significance of this has been expressed in setting up of the concept of "useful action" as the relation between the work performed and the amount of heat which must be supplied to the upper reservoir to gain it: $\eta = A/Q_u$.

Carnot clearly recognized that the technical problem consists, furthermore, in no less degree, in the removal of the heat collected in the lower reservoir, so that a new "useful action" expressed by $\eta = A/Q_1$ could be introduced with equal logic as a measure of the effectiveness. However, if only the coefficient of $\eta$ and the heat admitted to the system are given significance, it depends upon the *purely practical circumstance*; namely, that $T_u$ is always higher than the normal temperature of the earth's surface, that heat must be supplied to maintain $T_u$ with aid of exothermal chemical processes, while a corresponding arrangement is not required by the temperature $T_1$ since it is that of the earth's surface. If the earth's surface temperature were used as the higher temperature in the heat engine, the technical problem would not be the procurement of $Q_u$, but the removal of $Q_1$ *with the aid of endothermal processes*. In this case there would scarcely exist the same conditions for the conception of heat as a kind of energy transformable to others. The process then might be called "the production of work from cold."

Brillouin[14] has commented upon our suggestion that "calorique" be translated entropy in introducing his main thesis dealing with the very modern topic Information and Entropy:
"Cette interprétation ajoute évidemment une légère retouche moderne au texte original. Le calorique dont parle Carnot est un élèment qui se conserve, lorsqu'il est employé, dans une machine réversible (Carnot, p. 19) . . . La Traduction Brønsted-La Mer donne à ce passage une limpidité cristalline."

The reader's attention is also directed to an older publication of F. O. Koenig.[15] While we do not subscribe to one of Koenig's postulates, namely, that Carnot's work is based on the false caloric theory of heat, for the reasons detailed above, nevertheless, we fully agree with his main thesis:

"He (Carnot) stands at the beginning of thermodynamics with a constructive contribution of the first magnitude supplemented by a deductive achievement noteworthy for its prescience."

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[14] Leon Brillouin, "La vie, la pensée et la physico-chimie," Extrait des Cahiers de la Pleiade, No. XIII, Autumn 1951—Spring 1952 (Paul Dupont, Paris).

[15] Koenig, "On the significance of the forgotten thermodynamic theorems of Carnot," *Essays in Biology* (University of California Press, 1943), p. 277.

# The Tippe Top (Topsy-Turvy Top)

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(Received March 30, 1953)

Two fundamentally different explanations have been given in the literature to explain the "unusual" motion of a specially constructed spherical top in which rotation causes the center of gravity of the top to rise, the top turning 180° and finally spinning on its stem like an ordinary top. This independently derived analysis shows that the force due to sliding friction is in such a direction as to result in a torque which causes the angular velocity components to vary in a way which necessitates the rising of the center of gravity. This analysis, which emphasizes the physical picture behind the phenomenon, agrees with two previously published papers that friction plays the primary role. Some experimental evidence is given to support the present analysis.

A SPECIAL toy top whose behavior seems quite unusual has appeared both abroad and in the U. S. This toy, which is referred to as a "tippe top" or "topsy-turvy top," consists of a spherical body and stem with the center of gravity of the top below the center of curvature of the spherical body, as shown in Fig. 1. If the tippe top is given sufficient spin about its axis of symmetry with $\theta = 0$ initially it will turn such that $\theta$ increases and finally the top will spin on its stem like an ordinary sleeping top.

Two fundamentally different explanations have been written on the unusual behavior of this top. Synge[1] has maintained that friction seemed to have little effect on the motion of the tippe top and that its motion can be explained on the basis of dynamic instability of the top with no consideration of friction; whereas, both Braams[2] and Hugenholz[3] maintain that the force of friction gives rise to a torque which tends to raise the center of gravity and thus turn the top over. An explanation given by Jacobs[4] is that the friction increases the rate of precession and as a consequence causes the center of gravity to rise. This explanation was given in a letter, and since details on it are lacking no further comment can be made. Because of the fact that these different explanations have been made this note is being written, since in May, 1952, the writer had independently come to the same fundamental conclusion as given in the later publications of both Braams and Hugenholz, and in addition it has come to the attention of the writer that some people are still unaware of the published papers.[5] The detailed analysis is rather similar to those used by both Braams and Hugenholz, but it seems to be more direct and, in addition, puts more emphasis on the physical picture behind the phenomenon. Additional experimental evidence is given in support of the view that the unusual motion is due to friction.

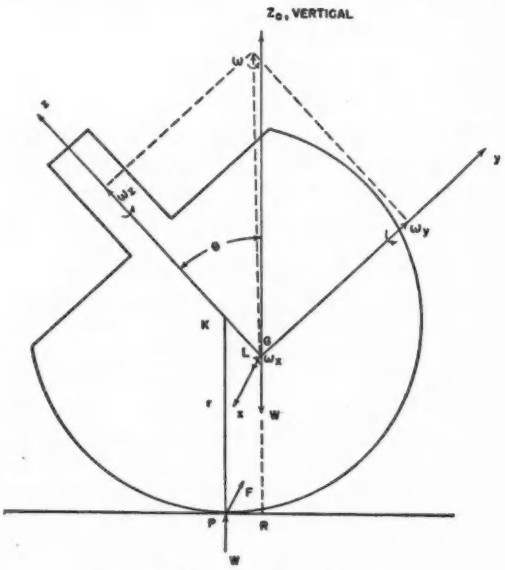

FIG. 1. Diagram of the tippe top.

In conjunction with Fig. 1 the following symbols are defined and relationships obtained:

[1] J. L. Synge, Phil. Mag. **43**, 724 (1952).
[2] C. M. Braams, Physica **18**, 503 (1952).
[3] N. M. Hugenholz, Physica **18**, 515 (1952).
[4] J. A. Jacobs, Am. J. Phys. **20**, 517 (1952).
[5] Letters to the Editor, The Johns Hopkins Magazine, February, 1953, p. 3.

$G$ is the center of gravity of the top.
$K$ is the center of curvature.
$L$ is the distance $GK$.
$r$ is the radius of curvature.
$xyz$ is a moving coordinate system such that the $z$ axis is coincident with the axis of symmetry and the $x$ axis is horizontal.
$\omega$ is the angular velocity of the $xyz$ coordinate system and for all practical purposes it is along the vertical since experimental observation of the tippe top easily verifies that $\omega_z=\dot{\theta}$ is small in comparison with $\omega$. Thus we have

$$\omega_y=\omega\sin\theta, \quad \omega_z=\omega\cos\theta. \tag{1}$$

$s$ is the spin of the top about the $z$ axis relative to the moving $xyz$ system. Experimental observations show that it is small in comparison with $\omega$ (see Fig. 4).
$P$ is the point of contact of the top with the surface.
$R$ is the projection of $G$ onto the horizontal supporting plane.
$F$ is the force of friction and the angle $\beta$ between it and the $-x$ direction is negligible for all practical purposes as will be discussed later.
$W$ is the weight of the top.
$g$ is the acceleration due to gravity.
$A$ is the moment of inertia about the $x$ or $y$ axes.
$C$ is the moment of inertia about the $z$ axis.

Before proceeding further it is instructive to point out an optical illusion observed under satisfactory conditions. If one spins the tippe top on a smooth shiny surface with sufficient light in the background it will appear that the top is not touching the supporting surface but that $T$, the lowest point of the top, is just above the surface and is slightly pointed, as shown in Fig. 2, where the top is shown in two different positions. This is the result of any motion in which the point of contact $P$ makes a circular path due to the rapid rotation of the top. The paths made by $R$ and $P$ are for all practical purposes concentric circles, although not necessarily as drawn in Fig. 2 (or 3).

It will now be shown that for all practical purposes $\rho$, the radius of the circular path made

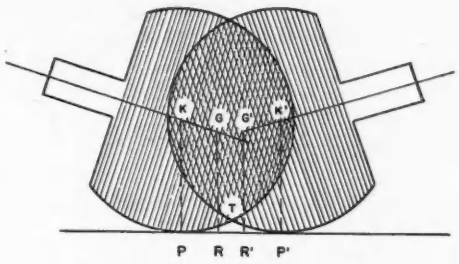


FIG. 2. Optical illusion that the top is not touching the supporting surface.

by $R$, is negligibly small and therefore one could consider that the top rotates about its center of gravity. It will also be shown that for all practical purposes $\beta$ is negligibly small and therefore $F$ is in the $-x$ direction. In Fig. 3 any initial horizontal motion given to the tippe top is neglected and thus the concentric circular paths of $P$ and $R$ are shown. In Fig. 3, $V_R$ is the horizontal motion of $G$, $V_P$ the horizontal motion of $P$ and $V_{P,R}$ is the horizontal motion of $P$ relative to $G$ or $R$. $V_{P,R}$ is given by

$$V_{P,R}=(L\omega+sr)\sin\theta.$$

The motion of $P$ due to $\omega_z$ is neglected since $\omega_z$ is comparatively small, as previously mentioned. From Figs. 1 and 3, we have

$$\rho=PR\sin\beta=L\sin\theta\sin\beta,$$
$$V_R=V_{P,R}\sin\beta.$$

The force of friction $F=\mu W$, where $\mu$ is the coefficient of sliding friction, balances the centrifugal reaction of $G$ (or $R$), and therefore

$$V_R=(\mu g\rho)^{\frac{1}{2}},$$

and thus we obtain

$$\sin\beta=\mu gL/(L\omega+sr)^2\sin\theta,$$
$$\rho=\mu gL^2/(L\omega+sr)^2.$$

The value of $\omega$ is, in general, so large that both $\beta$ and $\rho$ are relatively small. For example in the case of a home-made top $\beta$ was found to be less than 5° and $\rho$ less than $0.1L$ in the range $\theta=30°$ to $\theta=120°$ (just preceding its rising on its stem).[6] Approximate calculations that were made on

[6] In fact, the 5° value was rather extreme. In the range $\theta=0°$ to $\theta=90°$, $\beta<2°$ and $\rho<0.03L$.

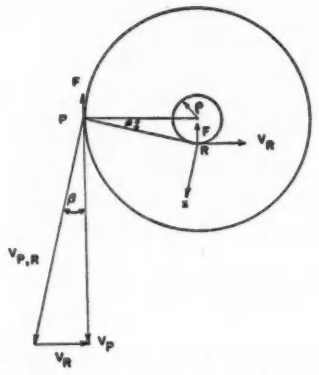


FIG. 3. The horizontal motion of $P$ and $R$.

some of the mass-produced plastic models also show that $\beta$ and $\rho$ are relatively small.

Now one can get a simple but crude physical picture of the unusual behavior of the tippe top by referring to Fig. 1. If $\omega$ is sufficiently large, which is the case if the top eventually turns over, then $\rho$ and $\beta$ are small, as has been shown, and one can consider that the body rotates about its center of gravity $G$ resulting in the force of friction $F$ acting in the $-x$ direction, i.e., into the plane of the paper. Thus, if $\theta<\cos^{-1}(L/r)$, the force of friction will result in a positive torque about the $y$ axis tending to increase $\omega_y$ and at the same time a negative torque about the $z$ axis tending to decrease $\omega_z$.[7] The over-all effect is a decrease of the ratio $\omega_z/\omega_y$, but $\omega_z/\omega_y=\cot\theta$, and thus $\theta$ must increase. Provided the moments of inertia are proper, then in the region $\pi/2\geq\theta\leq\cos^{-1}(L/r)$, $\omega_z$ could be considered to decrease at a faster rate than $\omega_y$ so that $\cot\theta$ decreases and thus $\theta$ must increase. Similarly if $\theta>\pi/2$ both $\omega_y$ and $\omega_z$ must decrease ($\omega_z$ becoming more negative); thus Eq. (1) requires a further increase in $\theta$. Thus $\theta$ increases until the stem touches the supporting surface. This is only a crude picture and does not explain all the effects but it does serve as a useful introduction to the more detailed equations.

The forces caused by friction and by the weight of the top result in a torque whose three components are $-WL\sin\theta-(\mu W)\times(r-L\cos\theta)\sin\beta$, $\mu W(r\cos\theta-L)\cos\beta$, and $-\mu Wr\sin\theta\cos\beta$. With $\omega$ sufficiently large, $\beta$ is small, and thus for practical purposes $\sin\beta=0$ and $\cos\beta=1$. Since $\omega_x$ and $\rho$ are small, one can to a sufficient degree of approximation consider the origin $G$ of the rotating $xyz$ coordinate system as fixed, and thus from Euler's equation[8] and the above torque components we have

$$A\dot\omega_x+(C-A)\omega_y\omega_z+Cs\omega_y=-WL\sin\theta, \tag{2.1}$$

$$A\dot\omega_y+(A-C)\omega_z\omega_x-Cs\omega_x=\mu W(r\cos\theta-L), \tag{2.2}$$

$$C\dot\omega_z+C\dot s=-\mu Wr\sin\theta. \tag{2.3}$$

With appropriate changes in coordinates and terms, these equations of motion are the same as those given by Hugenholz. The equations are the same as those for an ordinary symmetric top except for the torque components on the right. In the case of the ordinary top the torque component in Eq. (2.1) is of the opposite sign and the other two components are zero. From these considerations one would expect that if one decreased $\mu$ or increased $\omega$ sufficiently then motion more similar to that of an ordinary top should be observed. This was tried by Mr. J. E. Mapes by rotating the tippe top at high speeds on a well-lubricated smooth surface. It took the tippe top longer to turn over. In addition definite nutations were observed, whereas on an ordinary surface it nutated very little.

From Eqs. (1), (2.2), and (2.3) we obtain

$$\dot\omega_y=\dot\omega\sin\theta+\omega(\cos\theta)\omega_x$$
$$=[\mu W(r\cos\theta-L)-(A-C)\omega_z\omega_x+Cs\omega_x]/A; \tag{3}$$

$$\dot\omega_z=\dot\omega\cos\theta-\omega(\sin\theta)\omega_x=-(\mu Wr/C)\sin\theta-\dot s. \tag{4}$$

From these equations, one easily obtains

$$[\omega+((A-C)/A)\omega\cos^2\theta-(Cs/A)\cos\theta]\omega_z$$
$$=(\mu W/AC)[C(r\cos\theta-L)\times\cos\theta+Ar\sin^2\theta]+\dot s\sin\theta. \tag{5}$$

Now, from a consideration of the magnitude of the various quantities in Eq. (5), it will be shown that, if $\omega$ is sufficiently large, $\omega_z>0$ for the ordinary tippe tops. Since $(A-C)/A<1$ and $s$ is relatively small, therefore the coefficient of $\omega_z$ is

[7] This is the torque which could be held responsible for the small value of $s$ in comparison with $\omega$. The tippe top is unlike the ordinary top where the axis of rotation intersects the supporting surface at virtually the same point where the top touches the surface, explaining the negligible frictional torque in the case of an ordinary top.

[8] L. Page, *Introduction to Theoretical Physics* (D. Van Nostrand Company, Inc., New York, 1948), p. 123.

positive. Since $s$ is small, $\dot{s}$ is small and the other term on the left is obviously $>0$; therefore, $\omega_z=\dot{\theta}>0$. It is thus seen that $\theta$ increases until the stem touches the surface, which point then becomes the vertex of an ordinary-type top and, if $\omega$ is sufficiently large, the top rises and sleeps like an ordinary top. Further details of the rising on the stem is given by Hugenholz. Equation (5) also shows that $\omega_z$ is proportional to $\mu$, the coefficient of sliding friction. This has also been observed experimentally. In fact calculations were made on the home-made top for which the approximate physical quantities were known. The terms involving $s$ and $\dot{s}$ were neglected and $\omega$ was determined approximately for various values of $\theta$ by use of a stroboscope. The calculated and observed $\omega_z$ agreed favorably.

Since $\dot{\omega}_z$ is small, we obtain from Eq. (2.1)[9]

$$s=-WL/C\omega+((A-C)/C)\omega\cos\theta, \qquad (6)$$

and the angle $\theta'$ for which $s=0$ is given by

$$\cos\theta'=WL/\omega^2(A-C). \qquad (7)$$

From the above equations several conclusions can be drawn. If $\omega$ is sufficiently large then the direction of the spin relative to the rotating $xyz$ system is dependent on $A-C$. For example, if $A>C$, then $s$ will initially have the same sense as $\omega$ and, if $C>A$, then the spin rotation $s$ will be opposite that of $\omega$. Furthermore, $s$ reverses itself on passing $\theta'$. If $\omega$ is very large, $\theta'$ is nearly 90°. In addition as one decreases $\omega$, $\theta'$ decreases (provided $A>C$). In most cases $\theta'$ is a few degrees different from 90°. This is in disagreement with the statement made by Jacobs regarding the spin of the top relative to its figure axis when in the horizontal position ($\theta=90°$). These facts were all tested experimentally. Figure 4 gives an illustration of the observed carbon traces after having spun the tops on carbon paper.[10] The broken line is the equator of the top. The arrows shown on each trace indicate the order or sense in which the trace was made so that $s$ is in the sense opposite that given by the trace arrows. In general, in case of all the mass-produced plastic tippe tops which have been tested $A>C$. Two home-made tops were constructed. In one $A>C$ and in the other $C>A$. This last one was specifically constructed this way in order to test the theory. As expected, in case of the second home-made top, $s$ was opposite that found with the other tops.

Now, according to the theory advanced by Synge, the moments of inertia $A$ and $B$ about the $x$ and $y$ axes must at least not be equal in order for the tippe top to be unstable (when rotating with $\theta=0$) and thus turn over. In the present analysis and in the analyses previously reported by Braams and Hugenholz it is assumed that $A=B$. The experimental evidence seems to support that at least $A$ is approximately equal to $B$. Giving Synge the benefit of the doubt, then some of the tippe tops might possibly meet Case (a) described by him. But in the second home-made top even if $A$ and $B$ are not equal it could only fall under Case (c), which required stability according to Synge. It is not stable.

It must be remembered that Eq. (5) is based

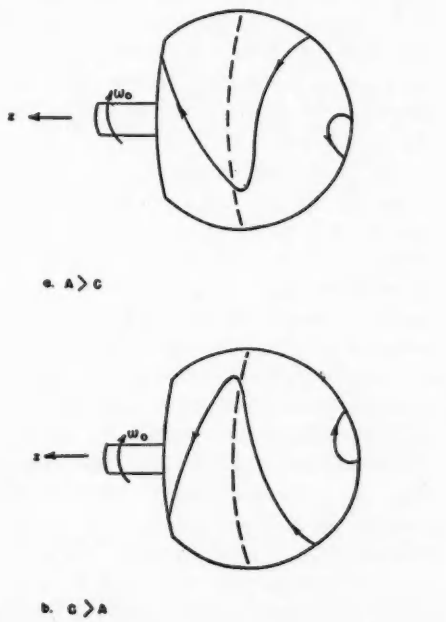


FIG. 4. Reversal in $s$, the spin relative to the rotating $xyz$ system, as shown by carbon traces. ($\omega_0$ is the direction in which the top was originally rotating when in the vertical position.)

[9] If the term involving $\sin\beta$ were not neglected, then Eq. (6) would be the same as Eq. (4) of Braams.

[10] Very often with the commercial models there is a fine spiral shape superimposed on the over-all form of the trace as shown here. This, as explained by Braams, is due to a small horizontal component of angular momentum.

on a force of friction in the $-x$ direction. Reference to Fig. 3 shows that, if $V_{P,R}=0$, then $F$ vanishes which results in $\omega_z=0$ and thus an equilibrium value for $\theta$. Setting $V_{P,R}=0$, we obtain $(L\omega+sr)\sin\theta=0$ which will occur if $\sin\theta=0$ or if $s=-L\omega/r$. Substituting this latter value of $s$ in Eq. (6) one obtains the same equilibrium values for $\theta$ as given by Hugenholz in Eq. (16). Further discussions on whether these equilibrium values are stable or unstable can be found in the papers by Braams and by Hugenholz.[11]

The author wishes to thank Dr. L. C. Roess for the helpful discussions during this study and Mr. James B. Smith for making the drawings.

[11] The stability described by Braams for what he calls a top of the second kind is correct if $e(=-L/r)>0$. If $e<0$ in a top of the second kind, then the stability conditions are just the opposite. The tops discussed here were of the first or second kinds.

## Reproductions of Prints, Drawings, and Paintings of Interest in the History of Physics

### 57. A Contemporary Portrait of Joseph Black

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(Received June 27, 1953)

A photograph of a very fine contemporary portrait of Joseph Black sculptured in wax by the famous modeler, James Tassie, is here reproduced.

A NUMBER of portraits of JOSEPH BLACK (1728–1799), the great chemist who laid the foundations of the quantitative science of heat, were reproduced in the fifth article in this series of historical reproductions.[1] However, this article failed to mention the white enamel profile medallion executed by JAMES TASSIE. Since the original wax model for this medallion has recently come into my possession, it seems worth while to reproduce a photograph of it in order to call attention to its existence. It is signed "Joseph Black, M.D. 1788" and is mounted on a black background in a contemporary polished walnut frame (6×7 in.). To me, it seems a more delicate composition than the paste medallion cast from it.

JAMES TASSIE (1735–1799), the famous gem engraver, executed many profile medallion portraits of his contemporaries, which are of great historic interest as well as artistic value (a collection of more than 150 is now in the Scottish National Portrait Gallery, Edinburgh). They were modeled in wax from life and cast in a hard white enamel paste.

JOSEPH BLACK, M.D. 1788.

[1] Am. Phys. Teacher, **7**, 123 (1939).

# The Recording of X-Ray Diffraction Patterns on Spheres

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AND

DAN MCLACHLAN, JR., *University of Utah, Salt Lake City, Utah*

(Received July 3, 1953)

In the teaching of the physics connected with the diffraction of x-rays, as well as the daily research practice of taking x-ray diffraction pictures, it is customary to take the pictures on flat x-ray film or upon sheets of film which has been curved into cylinders. In physics teaching this practice has very definite handicaps and appears to be somewhat indirect, because the theoretical treatment of the diffraction of x-rays is more directly connected to the geometry of spheres. We have, therefore, as a teaching aid, coated the inside surface of some hollow glass spheres with photographic emulsion and have recorded upon these spheres the diffraction of x-rays from small crystals located at their centers. Some of the results are shown in Figs. 1 a, b, and c.

## THE PREPARATION OF THE SPHERES

THE spheres used in this work were standard 200-watt inside-frosted incandescent light bulbs and which incidentally have a very uniformly thin wall thickness and a size of a little less than 10 centimeters in diameter. For the entrance and exit of the x-ray beam, two $\frac{3}{8}$-inch holes were drilled 180° apart on the equators of the spheres using carborundum with a hollow aluminum or brass drill, and the bulbs were cut off with a glass cutting saw about two centimeters below the equator.

Although the necessary skill in producing satisfactory coatings of photographic emulsions on the inside of spheres can only be acquired through practice, the following procedure is furnished as a guide. The emulsions used in this work were similar to a general x-ray emulsion described by Baker.[1] Ammoniacal silver nitrate was reacted with ammonium bromide and Knox unflavored No. 1 gelatine and allowed to ripen for 3 minutes at 40°C and then kept cool for 24 hours. The gel is then cut into small strips and washed in cold water until free of ammonia and halides. It is then melted and allowed to digest at 49°C for an hour or so—the exact time being determined by testing the film by exposure and observing for freedom from fog. Then the emulsion is cooled to await use.

To coat the spheres the emulsion is first heated to 42°C and about 10 cc poured through a linen cloth into a sphere. The filtration through cloth removes air bubbles. The sphere is then rotated until the inside surface is evenly coated, the excess emulsion poured out and the sphere quickly chilled by flowing tap water over its outside. The sphere is then air dried, and in order to prevent the emulsion from pealing off of the glass, the sphere is soaked in a 5-percent solution of glycerine in water and redried.

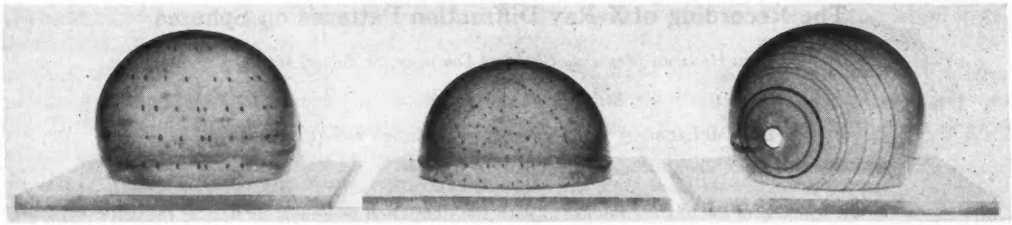
The x-ray pictures are taken by "cupping" the sphere over a carefully centered crystal on a goniometer so that the crystal is at the center of the sphere and the holes on the equator are aligned with the x-ray beam. Light protection may be furnished by a black box or by use of the shell of the General Electric rotation camera.

The results of this work are shown in Figs. 1 a, b, and c. Figure 1a is a rotation picture showing the usual "layer line" arrangement of spots, Fig. 1b shows a Laue picture with its interlaced rosettes and Figure 1c shows a powder picture with its Debye Scherer circles. The theoretical treatment of these results are discussed in the following paragraphs.

## THE DISTRIBUTION OF LAUE SPOTS ON THE SPHERE

To illustrate the problem in a simple way, let us assume that we have an orthorhombic crystal having unit cell dimensions $a$, $b$, and $c$ and that white radiation is sent down the $Y$ axis. It has been known generally that such an exposure of

[1] T. Thorne Baker, *Photographic Emulsion Technique* (American Photographic Publishing Company, Boston, 1941).



a b c

FIG. 1. Diffraction patterns on spheres: a. Rotation picture. b. Laue picture. c. Powder picture.

an orthorhombic crystal on a flat film produces a set of spots which appear to be located at the intersections of a series of curves resembling a rosette of four leafed clover patterns.[2] We should like to write the equations representing the locations of the possible maxima or spots on a spherical shell x-ray film.

Referring to Fig. 2 let us assume that the sphere is a glass bulb lined with sensitive x-ray emulsion and that a small crystal is located at its center $O$, with the x-ray beam going along the $Y$ axis through $O$ to $R$. Let the plane $UVW$ represent one of the planes in the family of planes which is diffracting x-rays in accordance with Bragg's concept. If $U$, $V$, and $W$ are the intercepts of the plane on the $Y$, $X$, and $Z$ axes, respectively, then from the definition of Miller indices,

$$OU=k/b, \quad OV=h/a \quad \text{and} \quad OW=l/c.$$

The distance $OP$, from $O$ perpendicular to the plane, is the interplanar spacing $d$, within the family of planes whose Miller indices are $h$, $k$, and $l$.

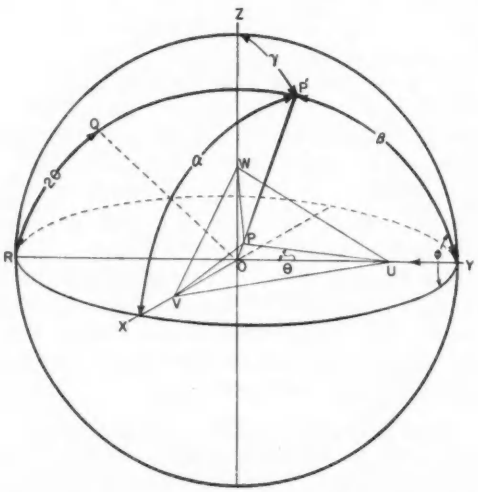



FIG. 2. The construction of angles useful in computing the positions of Laue spots.

There are two requirements for reflection besides Bragg's Law: (a) the angle of incidence equals the angle of reflection, and (b) the incident x-rays, the diffracted x-rays and the line $OP$ are in the same plane. The incoming x-rays strike the plane at $U$; and the angle between the incident rays and this plane is the angle $OUP$ which is designed as $\theta$. The diffracted rays make an angle $2\theta$ with the continued incident beam.

To simplify the discussion, the line $OP$ has been extended to $P'$, a point on the surface of the sphere. The great circle $YP'QR$ contains the point of entrance of the incident beam $Y$, the pole $P'$, and the point of exit of the diffracted beam $Q$. The arcs $P'Z$, $P'Y$, and $P'X$ are the angles of $\alpha$, $\beta$, and $\gamma$. Since the angles $VPO$, $UPO$, and $WPO$ are all right angles we obtain

$$\begin{cases} \cos\alpha = hd/a \\ \cos\beta = kd/a = \sin\theta \\ \cos\gamma = ld/c. \end{cases} \tag{1}$$

The great circle $YP'QR$ makes an angle $\Phi$ with the great circle $YXR$. Since $Q$ is the point at which a diffraction spot should appear on a spherical film it is our object to express $\theta$ as a function of $\Phi$ and the necessary cell constants and Miller indices of the spot in question.

From spherical trigonometry we have the

[2] See, for example, *The International Structure Factor Tables* (G. Bell and Sons Ltd., London, 1935), Vol. II, p. 644.

following equations relating to the three angles $A$, $B$, and $C$ of a spherical triangle with the opposite sides, $a$, $b$, and $c$:

$$\frac{\sin A}{a}=\frac{\sin B}{b}=\frac{\sin C}{c}, \tag{2}$$

$$\cos a=\cos b\cos c+\sin b\sin c\cos A. \tag{3}$$

Applying Eqs. (1) and (3) to the triangle $XYP'$ we get

$$\cos\alpha=\cos\beta\cos 90^\circ+\sin\beta\sin 90^\circ\cos\phi, \tag{4}$$

or

$$\cos\phi=\frac{\cos\alpha}{\sin\beta}=\frac{hd}{a[1-\cos^2\beta]^{\frac{1}{2}}}.$$

But since, for an orthorhombic system,

$$d=\frac{1}{[(h/a)^2+(k/b)^2+(l/c)^2]^{\frac{1}{2}}} \text{ and } \cos\beta=\frac{kd}{b}$$

we find

$$\cos\phi=\frac{h}{a[(h/a)^2+(l/c)^2]^{\frac{1}{2}}}, \tag{5}$$

$$\sin\theta=\frac{kd}{b}=\frac{k}{b[(h/a)^2+(k/b)^2+(l/c)^2]^{\frac{1}{2}}}. \tag{6}$$

Eliminating $(h^2/a^2+l^2/c^2)$ from Eqs. (5) and (6) we get the equation

$$\theta=\pm\tan^{-1}[ak\cos\phi/bh]. \tag{7}$$

Following this same precedure with the triangle $YZP'$ we get the equation

$$\theta=\pm\tan^{-1}[ck/bl]\sin\phi. \tag{8}$$

Equations (7) and (8) are the ones sought after and must be simultaneously satisfied to predict the location of diffraction spots on the sphere. Looking down the $Y$ axis from $R$ toward $Y$ the various values of $\phi$ appear as straight radii converging at $R$ as in Fig. 3 and the values of $\theta$ appear as concentric circles. Using this polar coordinate system, a plot of $\theta$ against $\phi$ using Eq. (7) with $h$ assigned the constant value 1 and $a=b=c$, produces the curves marked $a$ for $k=1$, $b$ for $k=2$, etc., and the opposing set $a'$, $b'$, $c'$, $d'$, $e'$; while the similar plot of Eq. (8) gives the curves $f$, $g$, $h$, $i$, $j$, and $f'$, $g'$, $h'$, $i'$, $j'$.

The points of intersection of these curves correspond to the simultaneous solutions of Eqs.

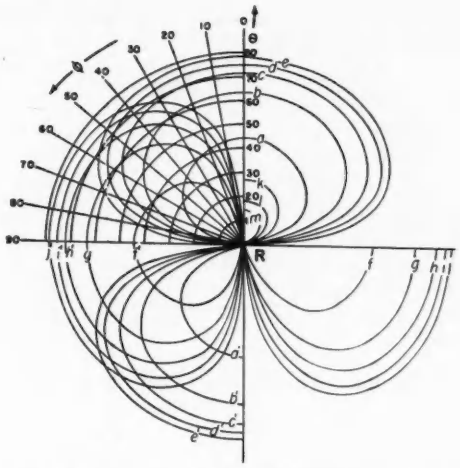



FIG. 3. The net for predicting the positions of some of the Laue spots.

(7) and (8) and therefore predict the values of $\phi$ and $\theta$ at which diffraction spots can occur for a cell in which $a=b=c$ and $h=l=1$. Similar curves are obtained keeping other indices constant; for example, the curves $k$, $l$, and $m$ are obtained when $k=1$ in Eq. (7) for successive values of $h$. These intersecting curves with spots at the intersections are clearly revealed on the spherical film such as is shown in Fig. 1b.

## THE DISTRIBUTION OF SPOTS ON A ROTATION PICTURE

Rotation pictures taken on a cylindrical film[3] have spots that are distributed in layers called the zero layer, first layer, second layer, etc., as though the diffracted x-rays had been confined to concentric cones wherein the axis of the cones are coincident with the axis of the cylinder. The layer lines are visible on a spherical film as shown in Fig. 1a. Designating as $\epsilon$ the angle between the equatorial plane and the cones it is our objective to solve for $\epsilon$ as a function of the crystallographic constants, the wavelength $\lambda$, and the conditions of photography.

Since rotation pictures are taken with monochromatic radiation, Bragg's equation must be satisfied

$$\lambda=2d\sin\theta. \tag{9}$$

[3] See, for example, W. P. Davey, *Study of Crystal Structure and its Applications* (McGraw-Hill Book Company, Inc., New York, 1934), p. 179.

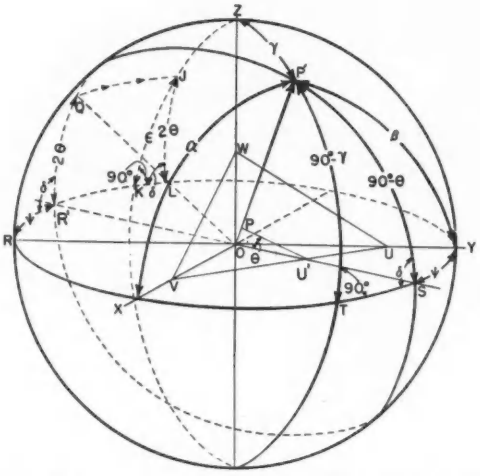



FIG. 4. The construction of angles useful in computing the positions of diffraction spots on rotation pictures.

For a crystal which is not rotating to satisfy Eqs. (7), (8), and (9) simultaneously, requires more than might happen except by chance; and it is therefore necessary to rotate the crystal. The angle between the $Y$ axis and the x-ray beam is designated $\psi$ in Fig. 4.

In Fig. 4 the construction and symbols are similar to Fig. 2 except that rotation of the crystal about the axis $OZ$ has required the addition of some angles. The x-ray beam coming in at angle $\psi$ penetrates the sphere at $S$, strikes the diffracting plane at $U'$ and continues through $O$ to $R'$, while the diffracted beam strikes the sphere at $Q$.

Applying Eq. (2) to the triangle $P'ST$ we have

$$\frac{\sin\delta}{\sin(90-\gamma)}=\frac{\sin 90}{\sin(90-\theta)}, \tag{10}$$

or

$$\sin\delta=\frac{\cos\gamma}{\cos\theta}. \tag{11}$$

Applying Eq. (2) to the triangle $JLK$ we have

$$\frac{\sin\epsilon}{\sin\delta}=\frac{\sin 2\theta}{\sin 90}, \tag{12}$$

or

$$\sin\epsilon=\sin 2\theta\,\sin\delta=\sin 2\theta\frac{\cos\gamma}{\cos\theta}$$

$$=\frac{2\sin\theta\cos\theta\cos\gamma}{\cos\theta}=\frac{2\lambda}{2d}\frac{ld}{c}=\frac{l\lambda}{c}. \tag{13}$$

When the x-ray beam strikes the axis of rotation of the crystal at right angles, the resulting picture is called a normal beam picture.. The values of $\epsilon$ for rotation about the $X$ and $Z$ axes are

$$\sin\epsilon=h\lambda/a, \tag{14}$$

$$\sin\epsilon=k\lambda/b. \tag{15}$$

Buerger[4] using a more general symbolism expresses Eqs. (13), (14), and (15) by the single equation

$$\sin\nu_n=n\lambda/t.$$

## THE POWDER PICTURES

In powder pictures the sample is about 300 mesh in fineness, and the unoriented crystals lie in all possible positions in sufficient numbers that Eqs. (7), (8), and (9) are easily satisfied by some crystals, even though the beam is monochromatic. The values of $\phi$ are not separated but the distinct values of $\theta$ appear as circles in Fig. 1a and in Fig. 4.

## ACKNOWLEDGMENTS

The authors wish to thank Dr. J. Hugh Hamilton, Head of the Engineering Experiment Station and Dr. John R. Lewis, Head of the Department of Metallurgy, University of Utah, for facilities and encouragement in this work and the Monsanto Chemical Company for a fellowship which made the work possible. Thanks are also due Dr. E. L. Quinn for advice and assistance.

[4] M. J. Buerger, *X-ray Crystallography* (John Wiley and Sons, Inc., New York, 1942), p. 95.

# NOTES AND DISCUSSION

## Doppler Effect Equation

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THE Doppler effect has long been a stumbling block for students of introductory physics. To describe all cases, a total of six different equations is necessary. This is too many to expect students to remember, and it is too time consuming to require students to derive the necessary equation for every problem.

The situation, in many respects, is similar to that in optics where three different equations are needed to describe the relations between object distance, image distance, and focal length for mirrors and for lenses. This has been simplified for mirrors and lenses by using one equation and one rule of signs to give the correct equation for any case.[1]

A simplification similar to that for mirrors and lenses can also be made for the Doppler effect equations. A single equation[2] which describes all possible cases of the Doppler effect is the following:

$$\frac{f_o}{V-v_o}=\frac{f_s}{V-v_s},$$

where $f_o$ is the frequency for the observer and $f_s$ the frequency for the source.

The component of the velocity of the observer along the line between observer and source is $v_o$, and the component of the velocity of the source along this line is $v_s$. The velocity of sound is $V$.

To transform this one equation into the correct equation for any special case the rule for signs is as follows: The velocity of sound at the observer is positive and its direction shows the positive direction. Either $v_s$ or $v_o$ is positive if directed along the positive direction, and negative if directed opposite to the positive direction.

To illustrate the use of this equation and rule of signs several cases may be considered.

*Case* (*1*).—Source and observer approaching each other. In this case $v_s$ is positive and $v_o$ is negative giving

$$f_o=f_s\frac{V+v_o}{V-v_s}.$$

*Case* (2).—Source and observer moving in the same direction. In this case $v_s$ and $v_o$ are both positive giving

$$f_o=f_s\frac{V-v_o}{V-v_s}.$$

If $v_o=v_s$, then $f_o=f_s$.

*Case* (*3*).—Observer at rest and source approaching at a speed $v_s=2V$. In this case $v_o=0$ and $v_s$ is positive giving

$$f_o=f_s\frac{V}{V-2V}=f_s\frac{V}{(-V)}=-f_s.$$

The frequency for the observer is the negative of the frequency for the source. The observer hears the sound reversed or backward *after* the source has passed him.

*Case* (*4*).—Bat flying toward a reflecting wall and listening to his own echo. Considering the image of the bat as the observer, $v_s$ becomes positive and $v_o=-v_s$ giving

$$f_o=f_s\frac{V+v_s}{V-v_s}.$$

The Doppler effect equation is easy to remember. It is symmetrical, with a relation applied to the observer on one side and the same relation applied to the source on the other side of the equality sign. Students easily remember both the equation and the rule of signs and can work problems without having to first derive the necessary equation.

The Doppler effect equation also applies when a wind is blowing. In this case $V$ represents that vector addition of sound velocity and wind velocity which has a direction along the line between the source and the observer. The vector $V$ is determined by drawing first the vector for the wind velocity and then with the head of this vector as a center drawing a circle of radius equal to the sound velocity. The line through the starting point parallel to the line between source and observer intersects the circle to give the value of $V$ to use in the equation.

An approximate correction for wind velocity[2] is to let $V=V_o+v_w$, where $V_o$ is the velocity of sound and $v_w$ is the component of wind velocity along the line between source and observer. The latter is positive if in the positive direction and negative if opposite to that direction.

The corrections for wind apply only when the wind velocity between the source and the observer is uniform.

[1] J. G. Winans, Am. J. Phys. **8**, 63 (1940).
[2] J. G. Winans, *Introductory General Physics* (Ginn and Company, New York, 1952), p. 279.

## A Note on the Multipole Expansion of the Scalar Potential

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A FORM of the expansion of the scalar potential in spherical harmonics has been derived in a manner that apparently does not appear in any of the available textbooks. It was found useful in the presentation of the topic in a course of lectures on electromagnetism and has certain advantages over other forms; for example, the values of the coefficients of the spherical harmonics are shown explicitly, and the number of independent components of each order of multipole moment is obvious. When this form is presented in conjunction with the conventional expansion in rectangular coordinates, a rather complete discussion of the topic can be given.

Consider a charge distribution $\rho(x)$ clustered about the origin. At an observation point $x$ outside the distribution (for present purposes) the scalar potential is given by

$$\Phi(x)=\frac{1}{\epsilon}\int_V\frac{\rho(x')d\tau'}{R}, \qquad (1)$$

where $V$ is a volume enclosing the charge, and

$$R=\left[\sum_{i=1}^{3}(x_i-x_i')^2\right]^{\frac{1}{2}},$$

the distance between the observation point $x$ and the "wandering" point $x'$.

In spherical coordinates

$$\begin{aligned}(x)&=(r,\theta,\varphi),\\(x')&=(r',\theta',\varphi').\end{aligned}\tag{2}$$

Introduce a coordinate system whose 3-axis is along the line joining $(x)$ and the origin. The directions of the 1- and 2-axes of the new system are immaterial. In the new system,

$$\begin{aligned}(x)&=(r,0,0),\\(x')&=(r',\alpha',\beta');\end{aligned}\tag{3}$$

$$\frac{1}{R}=\left[\frac{1}{r^2+r'^2-2rr'\cos\alpha'}\right]^{\frac{1}{2}}=\frac{1}{r}\sum_{n=0}^{\infty}\left(\frac{r'}{r}\right)^n P_n(\cos\alpha')\tag{4}$$

$$(r>\text{ any } r' \text{ in } V).^1$$

Thus in this special coordinate system

$$\Phi(x)=\frac{1}{\epsilon}\sum_{n=0}^{\infty}\frac{1}{r^{n+1}}\bar{M}_n,\tag{5}$$

where

$$\bar{M}_n=\int_V r'^n\rho(x')P_n(\cos\alpha')d\tau'.\tag{6}$$

This is not very useful as it stands, as it implies a new calculation for each observation point. However, use can be made of the reasonably well-known addition theorem of spherical harmonics which states[2]

$$P_n(\cos\alpha')=\frac{4\pi}{2n+1}\sum_{m=-n}^{n}Y_n^{m*}(\theta,\varphi)\,Y_n^m(\theta',\varphi'),\tag{7}$$

where $\alpha'$ is the angle between the two directions $(\theta,\varphi)$ and $(\theta',\varphi')$; and $Y_n^m(\theta,\varphi)$ are the normalized spherical harmonics,[2]

$$\int_{4\pi}Y_{n'}^{m'*}(\theta,\varphi)\,Y_n^m(\theta,\varphi)d\Omega=\delta_{nn'}\delta_{mm'}.\tag{8}$$

Substituting into $\bar{M}_n$ for $P_n(\cos\alpha')$, one can write

$$\Phi(x)\equiv\Phi(r,\theta,\varphi)$$

$$=\frac{1}{\epsilon}\sum_{n=0}^{\infty}\frac{1}{r^{n+1}}\left[\frac{4\pi}{2n+1}\right]^{\frac{1}{2}}\sum_{m=-n}^{n}Y_n^{m*}(\theta,\varphi)M_n^m,\tag{9}$$

where

$$M_n^m=\left[\frac{4\pi}{2n+1}\right]^{\frac{1}{2}}\int_V r'^n\rho(x')\,Y_n^m(\theta',\varphi')d\tau'.\tag{10}$$

If the term of order $1/r^{n+1}$ is identified with the contribution of the $2^n$-pole, then it is clear, since $n\geq m\geq -n$ and the $Y_n^m$ are independent, that there are $(2n+1)$ independent components of the $2^n$-pole moment; e.g., there are thus 5 independent components of the quadrupole moment.

With $M_n^m$ defined as above:

$$\begin{aligned}M_0^0&=\text{total charge},\\M_1^1&=-(\sqrt{\tfrac{1}{2}})(p_1+ip_2),\\M_1^0&=p_3,\\M_1^{-1}&=(\sqrt{\tfrac{1}{2}})(p_1-ip_2),\end{aligned}\tag{11, 12}$$

where $(p_1, p_2, p_3)$ is the dipole moment vector; and so on for the other $n$.

The extension to the calculation of quantum-mechanical expectation values of the $2^n$-pole moment operators is conveniently made through the spherical harmonic formulation, noting that these values vanish for odd $n$, and that the $(2n+1)$ components are now not all independent. A possible classical application is the calculation of the various multipole moments that give rise to a given (say measured) potential on the surface of some sphere. For example, if one knows $\Phi(A,\theta,\varphi)$, where $A$ is a constant radius then

$$M_1^m=\epsilon A^2\left[\frac{3}{4\pi}\right]^{\frac{1}{2}}\int_{4\pi}\Phi(A,\theta,\varphi)\,Y_1^m(\theta,\varphi)d\Omega,\tag{13}$$

which can be evaluated numerically, if need be.

[1] J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Company, Inc., New York, 1941), p. 173.
[2] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1951), pp. 52–54.

## Efficient Method for Cooling a Diffusion-Type Cloud Chamber

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PREVIOUSLY described Langsdorf diffusion-type cloud chambers[1,2] consume dry ice so rapidly that it is often necessary to replenish the supply before proper

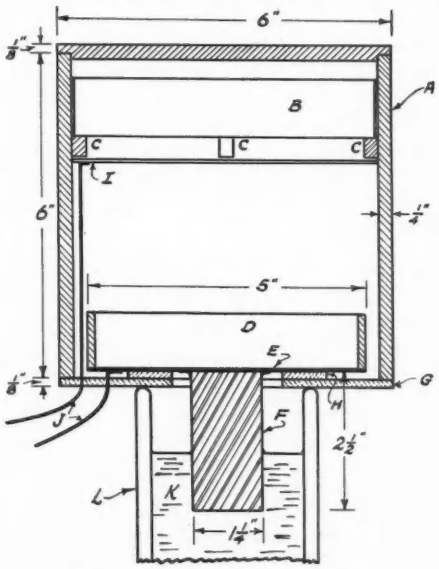


FIG. 1. Sectional view of cloud chamber.

temperature conditions have been attained, with the result that their operation is often unreliable. The chamber described here will operate for several hours without attention, displaying tracks due to both alpha and beta particles. A source of gamma rays or an x-ray tube operated in the vicinity produces the short curved paths characteristic of low-energy beta particles.

Figure 1 is a sectional view of the chamber drawn to scale so that the placement of the parts may be taken from the drawing where dimensions are not given. The chamber *A* is a Plexiglas cylinder with a one-quarter inch wall, provided with a removable top of the same material and fitted as shown. A ring of blotting paper *B*, supported on small Plexiglas blocks *C*, is moistened with methyl alcohol. A brass plate *E* painted dull black is the cold surface on which the vapor from *B* condenses. This plate is cooled by the alcohol-dry ice mixture *K* contained in a wide-mouthed vacuum bottle *L*. Thermal connection between the brass plate *E* and the cooling mixture is made by a solid brass cylinder *F* which passes through a hole in the masonite bottom *G*, of the chamber. Three small pieces of masonite *H* support the plate *E*. A ring of eighth-inch Plexiglas *D* about an inch high is placed on the plate *E*; this prevents the alcohol vapor from "falling" off the sides of the plate and produces a thicker sensitive layer. A circle of heavy wire *I*, held in place by friction, is one electrode of a sweeping field of about 400 volts; the other electrode is the brass plate. Connection is made to the power supply by the leads *J*. A 150-watt, 2×2 slide projector a few inches from the chamber provides ample illumination, if it is placed so that the light strikes the plate at nearly grazing incidence. Although no radioactive source is necessary, since the normal cosmic ray and other activity produce an abundance of energetic particles, a very spectacular display is produced by the point of a thumb tack which has been coated with a mixture of model airplane cement and material scraped from a luminous watch dial. It is important to remember that a source with too much activity will deplete the supersaturated layer, making the chamber inoperative.

[1] Science News Letter, Dec. 9, 1950.
[2] Scientific American, **184**, No. 1, 29 (January, 1951).

AMERICAN JOURNAL OF PHYSICS VOLUME 22, NUMBER 1 JANUARY, 1954

# LETTERS TO THE EDITOR

## Photoelastic Patterns without Crossed Polarizer and Analyzer

THE following fortuitous set of circumstances enabled me to see photoelastic strain patterns without the usual crossed polarizer and analyzer. As the sun was setting in the west, I sat at my desk facing south toward an open window. A plastic reel on my tape recording machine showed the multicolored patterns characteristic of strains. On taking the empty reel out of doors I found that the strain pattern disappeared if I faced east. Facing south the pattern reappeared only to disappear if I held the reel vertically. Sandpapering the underside of the reel caused the pattern to disappear. All of the above phenomena seem to be consistent with the following explanation: The light from the southern sky was polarized vertically by scattering. It entered the plastic and was reflected from its lower face. This reflection tended to produce horizontal polarization. This system replaced the usual one of crossed polarizers and the photoelastic effects due to double refraction in the plastic made themselves apparent.

ALBERT V. BAEZ

*University of Redlands*
*Redlands, California*

AMERICAN JOURNAL OF PHYSICS VOLUME 22, NUMBER 1 JANUARY, 1954

# ANNOUNCEMENTS AND NEWS

**Fundamentals of Physical Science.** Third Edition. KONRAD BATES KRAUSKOPF. Pp. 694+xii, Figs. 340, 16×23.5 cm. McGraw-Hill Book Company, Inc., New York 1953. Price $6.00.

This volume tells the story of man's struggle for understanding of his physical environment from Ptolemy to Einstein. It encompasses the physical world from electrons to galaxies. In a way, the book is a history of the development of science, but it contains much technical information as well. It was written primarily for use as a textbook in a general science course intended for students in a nonscience curricula. Material is taken from the fields of physics, chemistry, astronomy, and geology. These are remarkably well organized into a coherent whole in such a way that there are few "breaks" in the continuity of the text. At the proper level, one should be able to build an excellent course about this book.

There is no attempt at rigor. Mathematics is used only when an idea can be expressed in no other way and is then confined to the concepts of ratio and proportion in nearly

all cases. For this reason, the book should make excellent material for the general reader with an interest in science. In the words of the author, "all that is needed in the way of preparation is a lively curiosity and a willingness to make some effort to train the mind in an accustomed way of thinking."

The scientific approach is emphasized throughout the book. The author describes the scientific method as consisting of three steps: (1) observation, (2) generalization, and (3) checking by further observation. There are innumerable examples showing how this process led to scientific theory as it existed in the past and how certain of these hypotheses changed as more and better experimentation was done. Nearly all the "fundamental" ideas are developed in this way. More complicated concepts are always referred back to these "fundamentals." In my opinion, this continual referral to basic principles is one of the secrets of good teaching.

If one may interject a personal note, I will say that I enjoyed reading this book myself. I believe anyone would so regardless of scientific background. There are remarkably few errors, technical or otherwise. The area of material covered is so great that there is information to be gained for nearly everyone. On this account, the book could be used for reference in the study of either physics or chemistry.

One chapter deserves special mention. In the chapter on "Carbon Compounds," the fundamentals of organic chemistry are presented more simply and clearly than this reviewer has encountered elsewhere.

A useful addition to the second edition is a list of available visual aids to be used in connection with the material in the book.

R. M. PRICE
*University of Illinois*
*Chicago Undergraduate Division*

---

**Commentary on the Effect of Electricity on Muscular Motion.** LUIGI GALVANI. Translated by Robert Montraville Green. Pp. 97+xx, Figs. 4, 10.5×23.5 cm. Elizabeth Licht, 30 Hillside Avenue, Cambridge 40, Massachusetts, 1953. Price $4.00.

Electric currents were studied from 1729 on, and the 18th century saw important work in electrostatics. Yet frictional generators and Leyden jars were not adequate current sources for the early 19th century work of Ampère, Faraday, and their contemporaries, work that led directly both to Maxwell's formulation in electromagnetism and the concept of the atomicity of charges in matter. Thus, the invention of the voltaic cell was a step of utmost importance in the history of physics. And, it was Galvani who turned Volta's attention from marsh gas to "animal" electricity, by the publication of his paper "De viribus electricitatis in motu musculari commentarius," in 1791.

That paper was republished in 1792 by Galvani's nephew Giovani Aldini, together with an introductory commentary by Aldini and an exchange of letters between Bassano Carminati and Galvani concerning Volta's work. The present translation is of the Aldini book, with Aldini's annotations on Galvani's paper removed and some modern annotations added to Aldini's commentary. In addition, there is an introduction by Galvani's modern "academic heir," Professor Giulio C. Pupilli, of Bologna.

Galvani, professor of anatomy at Bologna, chose a physiological explanation of the phenomena he observed, while Volta, professor of physics at Pavia, chose the more fruitful path of concentrating attention upon the metal objects involved. In this sense Galvani was wrong, yet to those interested in teaching the history and development of ideas his work inevitably occupies an important place, and this translation is well worth their attention. The previous partial translations are not satisfactory, both because of their lack of completeness and their dubious sources: for example, the one in Magie's *Source Book in Physics* was translated from a German translation of the original with the unavoidable errors that accompany such a procedure.

It must be remembered that not only did the material translated here originate with an anatomist, but that this edition was prepared by persons primarily interested in the history of anatomy, not the history of physics. Thus one must not take too seriously the characterization of Aldini's commentary as "an introduction to electricity," or the modern footnotes that tell us Thales discovered the amber effect and that Volta invented the electroscope and condenser.

Another edition of the Galvani paper is scheduled for publication in October, 1953, by the Burndy Library and, hence, should be available by the time this review is published. It will probably be a more useful edition for physicists.

DUANE H. D. ROLLER
*Harvard University*

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**Microwave Spectroscopy.** WALTER GORDY, WILLIAM V. SMITH, AND RALPH F. TRAMBARULO. Pp. 446+xii. John Wiley and Sons, Inc., New York, 1953 (Structure of Matter Series). Price $7.50.

This book's claim to be the first written on the subject is an accurate one to the best of the reviewer's knowledge. The preface lists three aims. One is to provide a conveniently available source of much of the precise information which has been obtained through microwave spectroscopy. The second is to facilitate analysis of microwave spectra by including tables and formulas in convenient forms. And, finally, the book is written as an aid to the beginner in the field who wishes to learn something of the experimental techniques of microwave spectroscopy. That the first two aims were not taken lightly by the authors is indicated by the 67 pages of appendices tabulating experimental results and quantities to be used in analysis of spectra.

Whether one has worked in microwave spectroscopy or not, he is likely to find it a fascinating subject if only because it is a meeting ground for a great many of the increasingly less well-defined regions of physical science. The authors point out that physics, chemistry, electronic

engineering, and astronomy are all involved in either the technique or the applications or both. Such straddling of border lines calls for considerable versatility on the part of the authors, and it makes the problem of reaching all of the prospective readers a truly challenging one. However, a situation of this kind therefore presents a real place for a single book which makes the effort to tie it all together, and authors who take themselves away from their researches to tackle such a complex and, surely, at times disheartening task merit our fullest gratitude.

Perhaps the most fascinating aspect of the growth of microwave spectroscopy as a branch of science is its apparent illustration of the converse of a proverb, for it was surely the World War II invention of radar which mothered the postwar molecular researches using microwaves and, thus, the ultimate necessity for this book. Viewing the subject in this way, one can arrive at an operational definition of microwave spectroscopy, but Gordy, Smith, and Trambarulo include topics which might not be admitted even by the fairly broad criterion of use of techniques derived from radar.

The book begins quite properly with a chapter on microwave components and microwave spectrographs. There is, of course, treatment of molecular rotational spectra, inversion spectra, hyperfine interactions, and quadrupole interactions, as well as of the influence of the Zeeman and Stark effects for gases; both electric and magnetic dipole transitions are discussed. In addition, solids and liquids are treated, but here limitation of the discussion to sharp line spectra eliminates dielectric absorption, and only paramagnetic resonance receives attention. Not only are the paramagnetic salts and organic free radicals taken up, but the resonances associated with lattice defects, as in irradiated materials, are briefly mentioned, as are conduction electron resonances in metals. Semiconductor resonance was discovered too late to make the first edition of the book. Probably the only major topic omitted which could even remotely have been associated with the field is nuclear paramagnetic resonance or nuclear induction; this topic is justifiably considered to be material for a book in itself. A somewhat surprising inclusion is pure quadrupole resonance of the nucleus, on the grounds that, even though none has yet been observed in the microwave region, some pure quadrupole resonances ought to fall there.

The text creating these topics, as well as some material on the chemical bond, occupies 335 of the 446 pages, and it is perhaps best characterized as a reasonably well-organized and coherent guide to the extensive bibliography contained at the end of the book. In addition, there are references at the end of each chapter, which help to make this book useful to anyone who wants to gain a working knowledge of the field and who needs a place to start. The scientist who enters microwave spectroscopy for the first time and who has this book as his guide will find that the authors have indeed performed him an outstanding service.

G. E. Pake
*Washington University*

## Practical Aids for Teachers of Physics

### Improvisations

Professor Louis Weber, *Colorado A. & M. College*, Fort Collins, Colorado, spent the year 1952–1953 as Fulbright Lecturer in the College of Arts and Sciences, Baghdad, Iraq. He found himself much less liberally supplied with demonstration equipment and convenient storage rooms than in the United States. He therefore improvised many lecture demonstrations in which student participation was essential. Here are some of his suggestions:

1. *Dimensions.*—Hand a hammer and your watch to a student as he stands before the class and ask him what the objects suggest. Some of the brighter students will associate the head with mass; the handle with length, and the watch with time. (This idea came from the meeting of the American Physical Society when Dr. Condon received the gavel and time clock from the retiring president, Dr. Burgess in 1938 at Washington, D. C.)

2. *Sound wave.*—The first row of students in the lecture room stand and place their hands on the back of the students in front of them. The lecturer then pushes rather vigorously on the back of the last man in the line. Characteristics of wave motion can be pointed out to the class as they watch their fellow students experience a wave motion.

3. *Decibels.*—Let one student strike his fist regularly on his desk. Now at a given signal, he strikes both fists simultaneously. The level of intensity is now three db higher. Similarly, the whole class can repeat the experiment and the db change will of course be the same. Greater levels can also be demonstrated by all the students shouting. Whispers, low talking, conversation, and shouting, are about 0.001, 0.1, 10, and 1000 microwatts, respectively, or a total interval of about 60 db.

4. *Articulation.*—Call out vowel and consonant lists such as are suggested by Fletcher in *Speech and Hearing*. From the number of correct vowel and consonant sounds understood, the auditorium can be classed as satisfactory, excellent, or poor, or about 75, 85, or above, and 50 percent or less, respectively.

5. *Reverberation period.*—All the students clap their hands for several seconds to fill the room with sound. At a given signal, the sound is stopped, and the period determined for the sound to drop to zero level.

6. *Temperature and conduction.*—If asked to touch several objects on the lecture table, a student invariably comes to the conclusion that some are at a higher temperature than others even though the objects have come to temperature equilibrium.

Professor Julius Sumner Miller writes of the desirability of using apparatus to demonstrate collision phenomena that is on a scale large enough for a class to see clearly. His suggestion calls for an experiment on a heroic scale, using bowling balls about 9 inches in diameter, weighing 16 pounds each, in place of the 1- or 2-inch spheres that are ordinarily purchased as laboratory apparatus. In Los Angeles, the usual price of used bowling balls is apparently

$5.00 each, but Mr. Robert Meyers, Acme Billiard Supply Company, 2270 W. Washington Blvd., Los Angeles, California, is willing to sell them for educational purposes for $2.50 each. On request and for an additional charge, balls will be turned on a lathe to remove roughnesses.

Although the balls are not as elastic as steel, they compensate for this in the scale of operations which they permit. A suitable suspension is a clothes-line, 10 feet long. A turn-buckle should be included in each of the bifilar strings for adjustment.

Mr. Miller reports that although he had had this use of bowling balls in mind for several years, he saw it for the first time in operation at El Camino College, Lawndale, California, where the demonstration was prepared by Mr. Thomas N. Wilson. (Contributed by PROFESSOR JULIUS SUMNER MILLER, *2116 Benecia Avenue, West Los Angeles, California.*)

## Questions on Atomic Physics

The following examination paper was used in an introductory course in atomic and nuclear physics. (Contributed by ROBERT L. WEBER, *The Pennsylvania State College.*)

*Note.*—Put your name and your instructor's name on cover of "blue book." Start your answer for each question at top of a new page. Answers will be judged on their correctness, completeness, and clarity.

1. What significant information about the nature of matter and energy was deduced from investigations of each of the following? (20%)
   (a) the photoelectric effect
   (b) scattering of alpha particles by thin foils
   (c) the Compton effect
   (d) diffraction of electrons by crystals.
2. The Bohr theory predicts that the hydrogen atom can exist only in energy levels given by the expression $E=-2\pi^2me^4/(n^2h^2)$, where $n=1, 2, 3, \ldots$.
   (a) What are the hypotheses (assumptions) in the Bohr theory of the atom? (15%)
   (b) What is the relationship between the energy levels and the observed spectrum of the hydrogen atom? (10%)
3. Name three ways in which x-rays are absorbed in matter. (15%)
4. Answer any FOUR of the following SIX questions: (40%)
   (a) Calculate the wavelength of light that has just sufficient energy to remove a photoelectron from the surface of molybdenum (work function is 4.2 electron volts).
   (b) What is the maximum frequency of x-rays produced by an x-ray tube operated at 50 000 volts?
   (c) In a certain hydrogen atom the electron is in the energy level $n=4$. If this electron loses energy by radiation going from $n=4$ to $n=1$, what is the maximum number of photons it can emit? The minimum number? (Justify your answer.)
   (d) Justify the following statement: "The observed fact that the lines in the spectrum of hydrogen are very sharp is excellent evidence that all electrons have exactly the same charge $e$."
   (e) The kinetic energy of an electron may be written as $mc^2-m_0c^2$. What is the kinetic energy of an electron travelling with a speed $(\sqrt{3}/2)c$? Express your answer in ergs and in electron volts.
   (f) An electron having negligible kinetic energy meets a proton and combines with it to form a neutral hydrogen atom in the ground state. What is the maximum frequency of photon which can be emitted?

Mass of electron at rest $=9.11\times10^{-28}$ g.
Charge of electron $=4.80\times10^{-10}$ statcoulomb.
Planck's constant $=6.6\times10^{-27}$ erg-sec.
Speed of light in free space $=3.0\times10^{10}$ cm/sec.
Rydberg constant for hydrogen $=109\,677.7$ cm$^{-1}$.
1 volt $=1/300$ statvolt.
1 coulomb $=(1/3)\times10^{-9}$ statcoulomb.

## Telling Physics to the Public

"Communication has become an irksome two-pronged problem for the scientist."[1] In an attempt to bring this problem to the attention of our physics students, we have for the past two years conducted a Physics Fair which has had as its theme, "Telling Physics to the Public."

Early in the semester the students are given instructions for preparing a paper on some topic in the field of physics. The following is selected from a recent instruction sheet:

"The paper must be complete, accurate, and simple; and must not take more than 10 minutes to read. It should explain some principle of physics that can be demonstrated with apparatus that we have in the department or that can be built at reasonable cost. You are to use as few words as possible to tell an interesting story that can be understood by one who has not had a course in physics.

On Tuesday evening, March 31 you are to give this paper, without, notes, before a physics department "open house" to which the public will be invited.

From one to three students will have the program in each room. All our classrooms and laboratories will be available. The programs will begin at 7:30 p. m. and will be repeated each half-hour.

Each visitor attending will be handed a score sheet on which he will be asked to evaluate your attempts at telling physics to the public.

It is desirable that each student spend sufficient time in selecting and preparing his demonstration and paper. You may consult staff members, fellow students, and books in the physics library for further suggestions."

Two students later presented their papers and demonstrations on a television program over WDAF-TV in Kansas City. Attendance at the evening programs was good. (Contributed by WALLACE A. HILTON, *William Jewell College, Liberty, Missouri*).

[1] J. W. Hill and J. E. Payne, Science **117**, 403–05 (1953).

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